A liquid membrane process for uranium recovery.

An emulsion extraction process for recovering uranium from a WPPA feed solution containing uranyl cations wherein the WPPA feed is contacted with a water-in-oil emulsion which extracts and captures the uranium in the emulsion, wherein the improvement comprises adding excess oxidizing agent to the WPPA feed before or during the time that the feed is contacted with the emulsion. This results in both higher levels of uranium extraction and higher concentrations of uranium in the emulsion.
This invention relates to an improved process for recovering uranium from aqueous solution. More particularly, this process relates to an improved emulsion extraction process for recovering uranium from a WPPA feed solution which comprises adding excess oxidizing agent to the feed. Still more particularly, this invention relates to an improved process for recovering uranium from a WPPA feed solution containing uranyl cations which comprises adding excess oxidizing agent to the feed before or while it is contacted with the emulsion extractant.

Recovering uranium as a by-product from wet process phosphoric acid is well-known in the art. Phosphate rock is mined primarily to produce a high-phosphate containing fertilizer, the first step of which involves digesting the rock in sulfuric acid to produce a phosphoric acid solution which is known in the art as wet process phosphoric acid (WPPA). This WPPA contains uranium which can be recovered before the acid is further processed for making fertilizer. This uranium is present in the acid primarily as $\text{UO}_2^{2+}$ cations referred to in the art as uranyl ions, wherein the uranium is in the hexavalent, $+6$ state. In known processes for recovering uranium from WPPA, the uranium is extracted from the WPPA by contacting the WPPA with an extractant which is an oily, water-immiscible material consisting of a mixture of di-2-ethylhexyl phosphoric acid (D2EHPA) and trioctylphosphine oxide (TOPO) dissolved in an oily, organic liquid such as kerosene. The amount of uranium that the oily extractant can contain is limited by equilibrium conditions. This is quite low and is generally less than one gram of uranium per liter of extractant. The uranium enriched extractant is then separated from the WPPA and contacted with an aqueous solution containing a reducing agent such as ferrous ions in an acid such as
phosphoric acid, to convert the uranium to tetravalent U(IV) ions. The U(IV) ions are relatively insoluble in and are not re-extracted by the D2EHPA/TOPO-containing oil. This step results in stripping the uranium from the oily extractant into the aqueous reducing solution and the aqueous reducing solution is then further processed to recover the uranium. Thus, at least two different extraction operations are required. Typical of the prior art which teaches the recovery of uranium from WPPA by first contacting the acid with an oily extractant containing D2EHPA/TOPO, separating the uranium-enriched extractant from the uranium-reduced feed and then stripping the uranium from the uranium-enriched extractant with an aqueous reducing solution of ferrous ions in phosphoric acid are U.S. Patents 3,711,591 and 3,737,513.

Unfortunately, this well-known and commercially practised process for recovering uranium from WPPA suffers from many disadvantages, among which is a relatively low extraction efficiency ranging from about 1 to about 7. Extraction efficiency is defined as the ratio of the uranium concentration in the oily extractant to the uranium concentration remaining in the WPPA feed at extraction equilibrium conditions. Low extraction efficiency means that large quantities of expensive D2EHPA/TOPO extractant must be used and circulated with high concomitant losses of expensive reagents. Additionally large, expensive contacting vessels and settling tanks and pumps are required to handle large amounts of oily extractant. Another drawback of this process is due to the fact that as the temperature increases, the extraction efficiency decreases. For example, a report issued by the Oak Ridge National Laboratories (cf. Solvent Extraction of Uranium from Wet Process Phosphoric Acid, F. J. Hurst, D. J. Crouse and K. B. Brown, Report from Oak Ridge National Laboratory, April, 1969) disclosed that the extraction efficiency decreased from about 7 to about 1 when the extraction temperature, increased only from about 20°C to
60°C when uranium was extracted from WPPA using a solution of 0.2M D2EHPA and 0.5M TOPO in kerosene as the extractant. At a temperature of 40°C the extraction efficiency was 2. As a consequence, commercial processes must either operate at a temperature no higher than about 40°C or include more extraction stages to maintain a higher efficiency at the higher temperatures. The WPPA is produced at a temperature of about 60°C which means that the acid must be cooled down to about 40°C before being extracted or additional extraction stages must be used to maintain satisfactory extraction efficiency at the higher temperature. This naturally necessitates additional equipment and the use of considerable amounts of energy to cool the WPPA down to an economically viable extraction temperature.

It is known to use an emulsion process for recovering uranium from uranium-bearing WPPA streams. This emulsion process comprises contacting a uranium containing WPPA feed with globules of a water-in-oil emulsion comprising microdroplets of an aqueous interior phase dispersed in an oily, continuous exterior phase containing at least one transfer agent for selectively transferring the uranium from the feed into the interior phase of the emulsion wherein the valence of the uranium species is changed, thereby trapping the uranium in the emulsion. The uranium-enriched emulsion is then separated from the feed, the emulsion is broken and the uranium is recovered.

In a preferred embodiment of this process, the uranium is present in the WPPA feed as uranyl ion, the exterior phase contains a mixture of D2EHPA and TOPO as selective transfer agents for the uranyl ion and the interior phase of the emulsion contains a reducing agent which changes the uranyl to U(IV) ions, thereby trapping the uranium in the interior phase of the emulsion as uranous ions.

It has now been discovered that the liquid membrane emulsion extraction process known in the art is
improved if excess oxidizing agent is added to the uranyl ion-containing WPPA feed before and/or while the feed is contacted with the emulsion. By excess oxidizing agent is meant oxidizing agent in an amount greater than that initially added to the WPPA feed, if necessary, in order to ensure that all of the uranium in said feed is in the uranyl or hexavalent form and that any iron in the feed is in the ferric or trivalent form.

It is known in the art to initially oxidize or add oxidizing agent to the WPPA feed in order to ensure that all of the uranium is present therein as uranyl cations before contacting the feed with an extracting agent. In the liquid membrane extraction process, we have discovered that by adding to the feed excess oxidizing agent or oxidizing agent beyond that needed to initially ensure that the uranium in the feed is in the hexavalent state, one will obtain greater levels of uranium extraction and achieve higher levels of extracted uranium in the emulsion. Thus, this invention is an improvement in a liquid membrane emulsion process for recovering uranium from a WPPA feed containing uranyl cations which comprises the steps of (a) contacting, at a temperature of from between about 30 to 100°C, said WPPA feed with a water-in-oil emulsion comprising (i) an aqueous interior phase dispersed in (ii) an oily exterior phase immiscible with both said interior phase and said WPPA feed solution, said interior phase comprising an acid solution containing a reducing agent and said exterior phase comprising a surfactant-containing hydrocarbon solution of D2EHPA and TOPO which transfer the uranyl ion from the WPPA solution to the interior phase of the emulsion wherein said uranyl ion is reduced to the tetravalent U(IV) ion to form a uranium-rich emulsion, (b) separating the uranium-rich emulsion from the WPPA solution, and (c) recovering the uranium from the emulsion, wherein the improvement comprises adding excess oxidant to the WPPA feed before and/or during contacting the WPPA with the emulsion. In a preferred embodiment the contacting will take place in a plurality of zones.
The total amount of excess oxidant to be added will, of course depend on the feed and emulsion compositions and also on the process conditions. In general, the minimum amount of excess oxidant added to the feed will be that amount stoichiometrically needed to oxidize any U(IV) and ferrous ions that transfer back to the WPPA feed (due to leakage and/or breakage of the emulsion) to uranyl and ferric ions, respectively. The so-formed uranyl ions are then reextracted by the emulsion. The exact amount of excess oxidizing agent used will, of course, depend on both the amount of U(IV) and ferrous ion going back into the feed and the amount of uranium it is desired to extract from the WPPA. Any suitable oxidizing agents may be used in the process of this invention. Illustrative, but non-limiting examples of suitable oxidizing agents include chlorates, persulfates and peroxides such as hydrogen peroxide.

Contacting of the WPPA feed and emulsion is generally done in a countercurrent manner in a plurality of stages, each stage comprising at least one mixing zone and a settling zone, the mixing zone containing suitable means for mixing the WPPA feed with the emulsion. Illustrative, but non-limiting examples of suitable mixing means includes turbine and propeller mixers, static mixers, wire mesh, ultrasonic vibrations, etc. It is well-known that countercurrent extraction in a plurality of stages results in better extraction efficiency and requires less extracting agent or emulsion than a single stage. It is preferred that each stage contains a plurality of co-current mixing zones or compartments. Employing a plurality of smaller mixing zones in each stage as opposed to a lesser number of larger zones enables one to minimize the size of mixing equipment required to achieve a given amount of extraction as those skilled in the art will know based on the well known continuous-stirred-transfer-reactor (CSTR) theory.

'When the feed and emulsion are contacted in a mixing zone, a small amount of internal aqueous phase
of the emulsion leaks into the feed due to minor breakage of the emulsion from the mixing shear and rupture caused by internal phase swelling. Internal phase swelling is an osmotic effect resulting from difference in ion strength across the hydrocarbon membrane of the emulsion. Since the internal aqueous phase of the emulsion contains both extracted uranium in the tetravalent form and ferrous ion reducing agent, this leakage reduces the overall efficiency of the process by putting uranium back into the feed and by introducing iron into the feed which later requires that more oxidant be used to maintain the uranium in the feed in the hexavalent (uranyl) form.

In a preferred embodiment of this invention, the interior phase of the emulsion will be a phosphoric acid solution containing ferrous ions and the oily, water and feed-immiscible exterior phase of the emulsion will be a mixture of D2EHPA/TOPO in an aliphatic hydrocarbon which also contains a surfactant for forming and stabilizing the emulsion. The D2EHPA/TOPO in the exterior phase transports the \( \text{UO}_2^{2+} \) cations from the WPPA feed into the interior phase of the emulsion wherein the uranium is stripped from the D2EHPA/TOPO by the phosphoric acid and reduced to \( \text{U(IV)} \) ions by the ferrous ions and is thereby trapped in the emulsion.

Essential to the successful operation of the process of this invention is a suitable water-in-oil type of emulsion. It has been discovered that emulsions of the type disclosed in U.S. 3,779,907, are suitable for use in the process of this invention. These emulsions are referred to liquids include substantially aliphatic hydrocarbons such as kerosene and paraffinic hydrocarbons such as Norpar 13, SK-100, Low Odor Paraffin Solvent (LOPS) and Solvent Neutral 100 (S-100N) which are available from Exxon Chemical Company. It is understood, of course, that the hydrocarbon may contain one or more other hydrocarbons, halogenated hydrocarbons or higher oxygenated
compounds such as alcohols, ketones, acids or esters as long as the emulsion is stable and the exterior phase is immiscible with both the aqueous feed solution and aqueous interior phase and permits transferring the uranium from the feed to the interior phase of the emulsion. The exterior phase of the emulsion will contain from about 60-98 weight % of this hydrocarbon liquid, preferably from about 75-95% and most preferably from about 85-95 weight %.

As hereinbefore stated, the oily, water immiscible external phase of the emulsion will contain one or more oil soluble surfactants for forming and stabilizing the emulsion, but which will not prohibit transfer of the uranium through the exterior phase to the interior phase. Suitable surfactants may be selected from among oil soluble anionic, cationic, and nonionic surfactants. Surfactants that have been found to be particularly suitable for use in the process of this invention include various derivatives of polyisobutylene succinic anhydride (PIBSA) which includes, but is not limited to various polyamine derivatives thereof having the general formula:

\[ R_1 \rightarrow N \left[ \begin{array}{c} R_3 \ R_5 \ R_7 \\ C - C - N \end{array} \right] Y \]

wherein \( R_1, R_2, R_3, R_4, R_5, R_6, \) and \( R_7 \) and \( Y \) are hydrogen, \( C_1 \) to \( C_{20} \) alkyl, \( C_6 \) to \( C_{20} \) aryl, \( C_7 \) to \( C_{20} \) alkaryl radicals or substituted derivatives thereof; and \( x \) is an integer of from 1 to 100. \( R_3, R_4, R_5, R_6 \) and \( R_7 \) are preferably hydrogen, with \( x \) preferably varying from 3 to 20. The substituted derivatives are preferably oxygen, nitrogen, sulfur, phosphorus and halogen-containing derivatives. Various PIBSA-polyamine compounds that have been found useful in the practice of this invention include those taught in U.S. Patent No. 3,172,892.

A particular PIBSA polyamine derivative surfactant that has been found to be useful in the process of this invention is one wherein \( R_1 \) and \( R_2 \).
taken together to form an alkyl succinic radical and
wherein the surfactant is a compound having the general
formula:

\[
\begin{align*}
        & H - C \bigg( \bigg( C - CH_2 \bigg) \bigg) - C - C \bigg( \bigg( CH_3 \bigg) \bigg) - N - (CH_2 - CH_2 - N) - C - CH_3 \\
        & \text{wherein } m \text{ is an integer generally ranging of about } 10 - 60 \\
        & \text{and more preferably 40, thereby giving said preferred } \\
        & \text{polyamine derivative a molecular weight of about 2000.}
\end{align*}
\]

This surfactant will generally comprise from about 0.2 to
10 weight % of the exterior phase of the emulsion, prefer-
ably from about 0.5 to 5 weight % and still more prefer-
ably from about 1-3 weight %.

As hereinbefore stated, the external phase of
the emulsion must contain an agent capable of transferring
the uranium from the aqueous feed, through the oily
external phase to the interior phase. Transfer agents
found suitable for transferring cationic uranium species
containing hexavalent uranium (i.e. UO$_2^{2+}$) through the
external phase to the internal phase include a mixture of
oil soluble dialkyl esters of phosphoric acid and trialkyl-
phosphine oxide. In particular, a mixture of di(2-ethyl-
hexyl) phosphoric acid (D2EHPA) and trioctylphosphine
oxide (TOPO) are preferred for transporting uranyl (UO$_2^{2+}$)
through the external phase of the emulsion. This mixture
will not transfer uranium species wherein uranium exists
in the +4 valence U (IV) state. In general, the transfer
agent will comprise from between about 1-30 wt. % of the
exterior phase of the emulsion, preferably from about
2-18 wt. % and most preferably from about 2-6 wt. %.
When the transfer agent comprises a combination of D2EHPA
and TOPO they will be in said exterior phase in a molar
ratio ranging from about 1/1 to 10/1, preferably from 2/1
to 8/1 and, more preferably from about 2/1 to 7/1 of
D2EHPA/TOPO.
As hereinbefore stated, the interior phase of the emulsion will be an aqueous acid solution containing a reagent capable of changing the valence state of the uranium transferred through the oily, external phase to trap the uranium being removed from the aqueous feed where it is in the +6 valence state. This interior phase will be an aqueous acid solution containing a reducing agent to reduce the uranium to a +4 valence state. There should be enough reducing agent present in the internal phase to reduce the uranium ion transported therein. Illustrative, but non-limiting examples of suitable reducing agents include acid solutions of ferrous or chromous ions such as an aqueous solution of ferrous sulfate in phosphoric acid wherein the concentration of the ferrous ion ranges from about 8-50 grams per liter, preferably from 10 to 40g/liter and wherein the concentration of the phosphoric acid ranges from about 3-12 moles/liter and more preferably from about 5-8 moles/liter. The following reaction is believed to occur when reducing (UO$_2^{2+}$) with acidic ferrous sulfate:

\[
2\text{Fe}^{2+} + \text{UO}_2^{2+} + 4\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{U}^{4+} + 2\text{H}_2\text{O}
\]

It is important that the concentration of phosphoric acid in the internal phase be approximately the same as in the feed in order to avoid excessive swelling and ultimately destruction of the emulsion. As a matter of convenience, the internal phase may be prepared from the WPPA feed by adding iron thereto.

The interior phase will comprise from about 15-80 volume percent of the emulsion, preferably from 30-70 and most preferably from 33-60 volume percent, i.e., the volume ratio of the oily exterior or membrane phase to the aqueous interior phase of the emulsion will range from about 6/1 to 1/4, more preferably from about 2/1 to 1/2, and still more preferably from about 2/1 to 1/1.

The emulsions used in this invention may be prepared by any of the well known methods. Thus, a
solution comprising the components of the oily exterior phase is mixed with an aqueous solution which will form the interior phase under high shear conditions attained by the use of high speed stirrers, colloid mills, homogenizers, ultrasonic generators, mixing jets, etc.

As mentioned previously, the excess oxidizing agent can be added to the WPPA feed before it enters the extraction train, or it may be added in stages throughout the extraction sequence, or both. Thus, a portion of the excess may be added to the feed before it is contacted with the emulsion, with the remainder added at one or more points along the extraction train. Alternatively it may all be added to the feed prior to its being contacted with the emulsion or it may all be added to the feed at one or more points of the extraction train.

The invention will be more readily understood by reference to the examples set forth below.

**EXAMPLES**

**Example 1**

In this example, uranyl ion (UO$_2^{++}$) was laboratory batch extracted from an actual sample of central Florida WPPA comprising a 5.2M solution of H$_3$PO$_4$ containing 130 ppm of uranium as UO$_2^{++}$. The emulsion used to extract the uranium had the following composition:

- **External phase** - 2.91 wt. % D2EHPA, 0.88 wt. % TOPO and 5 wt. % of a PIBSA-THAM surfactant of the type disclosed in U.S. Patent No. 4,102,798, (made by reacting 1 mole of PIBSA having a molecular weight of about 1,300 with 1.9 moles of tris-hydroxymethyl amino methane) in LOPS:

- **Interior Phase** - a solution of 6M H$_3$PO$_4$ containing 30 g/l of ferrous ion; and the volume ratio of exterior to interior phase was 2/1.

The WPPA was filtered through a 1 m cartridge filter to remove the solid gypsum and some organics as solids. The WPPA, 1500 mL, was then added to the resin kettle of 10 cm I.D. fitted with four 1 cm vertical baffles and four evenly spaced marine propellers of 5.1 cm diameter. The temperature was increased to and controlled
at 60 ± 1°C with external heating tape and a Thermowatch
controller.

The liquid membrane emulsion was prepared in a Waring blender at 10,000 ppm for 4 min. using 333 mL of membrane and 167 mL of internal aqueous phase. The emulsion, 125 mL, for a feed to emulsion ratio of 12, was added to the resin kettle. Mixing at 600 rpm was then begun and was t = 0 for measurement of contact time. In the first run, only 0.068 grams of ammonium persulfate oxidant was added to the kettle which was just enough to insure that all of the uranium and iron in the WPPA feed were in the +6 and +3 valence state, respectively. This amount of oxidant was enough to give an initial concentration of oxidant in the feed of 0.001M. For run 2, 0.342 grams of oxidant were added initially (yielded initial conc. of oxidant of 0.005M) and another 0.342 grams after 10 minutes. In run 3, 0.342 grams were added initially, followed by another 0.342 grams after 20 minutes.

Samples of the dispersion were taken during agitation through a stopcock in the bottom of the resin kettle at various contact times. These samples were allowed to phase separate and aliquots of the raffinates were analyzed for uranium content. At the completion of extraction, a sample emulsion was coalesced to isolate internal phase for uranium analysis by X-ray fluorescence spectroscopy.

The results of these runs are set forth in Table I and illustrate a significant improvement in extraction efficiency using the process of this invention.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>(NH₄)₂S₂O₈ added to Feed, grams</th>
<th>Total Contact Time, Min.</th>
<th>U in Raffinate µg/g</th>
<th>Extraction %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.068</td>
<td>0</td>
<td>122</td>
<td>73</td>
</tr>
<tr>
<td>2</td>
<td>0.342</td>
<td>0</td>
<td>122</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>0.342</td>
<td>10</td>
<td>12</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>0.342</td>
<td>20</td>
<td>7</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>0.342</td>
<td>30</td>
<td>8</td>
<td>94</td>
</tr>
<tr>
<td>6</td>
<td>0.342</td>
<td>10</td>
<td>12</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>0.342</td>
<td>20</td>
<td>8</td>
<td>94</td>
</tr>
<tr>
<td>8</td>
<td>0.342</td>
<td>30</td>
<td>7</td>
<td>94</td>
</tr>
<tr>
<td>9</td>
<td>0.342</td>
<td>10</td>
<td>12</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>0.342</td>
<td>20</td>
<td>8</td>
<td>94</td>
</tr>
<tr>
<td>11</td>
<td>0.342</td>
<td>30</td>
<td>7</td>
<td>94</td>
</tr>
<tr>
<td>12</td>
<td>0.342</td>
<td>10</td>
<td>12</td>
<td>90</td>
</tr>
<tr>
<td>13</td>
<td>0.342</td>
<td>20</td>
<td>8</td>
<td>94</td>
</tr>
<tr>
<td>14</td>
<td>0.342</td>
<td>30</td>
<td>7</td>
<td>94</td>
</tr>
<tr>
<td>15</td>
<td>0.342</td>
<td>10</td>
<td>12</td>
<td>90</td>
</tr>
<tr>
<td>16</td>
<td>0.342</td>
<td>20</td>
<td>8</td>
<td>94</td>
</tr>
<tr>
<td>17</td>
<td>0.342</td>
<td>30</td>
<td>7</td>
<td>94</td>
</tr>
</tbody>
</table>
In an actual commercial extraction operation, the internal phase of the liquid membrane will contain tetravalent uranium, as U(IV) ion, to a loading in a range of about 6 to 12 g/L. Therefore, extraction of uranium from the WPPA was done with a preloaded emulsion whose internal phase contained 10 g/L of uranium as U^{4+}. The experimental conditions were the same as in Example 1. The results given in Table II show that no extraction was observed without added oxidant, whereas with added oxidant 47% of the uranium was extracted after 25 minutes contact time. These results demonstrate the significant and surprising improvement provided by the addition of oxidant during LM extraction of uranium.
### TABLE II

EFFECT OF ADDED OXIDANT ON URANYL ION EXTRACTION FROM
WET PROCESS PHOSPHORIC ACID WITH LOADED LM EMULSION

<table>
<thead>
<tr>
<th>Run No.</th>
<th>(NH₄)₂S₂O₈ added to Feed, g*</th>
<th>Total Contact Time, Min.</th>
<th>U in Raffinate µg/g</th>
<th>Extraction %</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0</td>
<td>5</td>
<td>131</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0.342g</td>
<td>10</td>
<td>76</td>
<td>42</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>15</td>
<td>73</td>
<td>44</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>20</td>
<td>79</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>0.342g</td>
<td>25</td>
<td>69</td>
<td>47</td>
</tr>
</tbody>
</table>

*NOTE: Oxidant added at end of preceding time period (i.e., 0.342g added after 5 min. and after 20 min. contact time).
EXAMPLE 3

More related to commercial practices, extraction was also carried out in a continuous contacting system comprising one extraction stage which contained five cocurrent, cascading mixing compartments. Each compartment was a cube of one liter capacity containing a marine propeller mixer. Pretreated WPPA and fresh LM emulsion were fed into the first compartment wherein a dispersion of LM emulsion in the continuous WPPA phase was formed by the shear of the marine propeller-stirrer contained in each compartment. The resultant dispersion cascaded through each successive compartment by overflow after a finite contacting period. Finally, the dispersion overflowed from the last compartment into a settler to allow disengagement and separation of the loaded LM emulsion from the WPPA raffinate phase.

Commercial WPPA was oxidized in polyethylene lined, 55 gal. drums with hydrogen peroxide and pumped through a 1 m polypropylene cartridge inline filter to a 3 L vessel. This vessel was a preheater which increased the temperature of the pretreated WPPA to 60-70°C. The acid was then fed via a peristaltic pump (all fluids were transferred with peristaltic pumps) to the continuous contacting system described above.

The detailed conditions of the experiments are given in Table III.

Samples of raffinate from each mixing compartment were analyzed for uranium content by inductively coupled ion plasma emission spectroscopy.

As seen from the results presented in Table III, a similar improvement in extraction of uranium from WPPA was obtained by the addition of oxidant to WPPA feed during extraction. In this case a 2.5M ammonium persulfate solution was added to the fourth mixing compartment at a flow rate of 0.2 ml/min. In Run 5, with no added oxidant, the extraction efficiency at 50 min. contact time was 63%, whereas, with added oxidant in Run 6, the extraction efficiency was 68%. This significant improvement was corroborated by the replicate experiment Run 7.


### TABLE III

**EFFECT OF ADDED OXIDANT ON CONTINUOUS EXTRACTION**

**Conditions:**

- feed – 30% P₂O₅ Central Florida WPPA, [U] – 130 g/g
- membrane – 3 wt. % surfactantᵃ, 2.91 wt. % DEHPA, 0.88 wt. % TOPO in Norpar-13
- internal phase – 30 g/L Fe(II) in 6M H₃PO₄
- F/E – 10, M/IR – 2
- mixing rate – 600 rpm, temp. – 60°C

<table>
<thead>
<tr>
<th>Run No.</th>
<th>(NH₄)₂S₂O₈ᵇ</th>
<th>U Extraction Efficiency at Various Contact Times, Min.ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>0.005</td>
<td>39</td>
</tr>
<tr>
<td>7</td>
<td>0.005</td>
<td>37</td>
</tr>
</tbody>
</table>

ᵃA PIBSA-polyamine surfactant of the type disclosed in U.S. 3,172,892 made by reacting 1.3 moles of PIBSA of a molecular weight of 1,000 with 1 mole of tetra-ethylene pentamine.

ᵇ(NH₄)₂S₂O₈ was added to fourth compartment.

ᶜEach 10 min. of contact time represented one mixer compartment.
1. An emulsion process for recovering uranium from a WPPA (wet process phosphoric acid) feed solution containing uranium ions in the hexavalent form wherein excess oxidizing agent is added to said WPPA solution, said process comprising:

   (a) contacting said WPPA feed with a water-in-oil emulsion comprising (i) an aqueous interior phase dispersed in (ii) an oily exterior phase immiscible with both said interior phase and said feed, said interior phase comprising an acid solution containing a reducing agent and said exterior phase comprising a surfactant-containing hydrocarbon solution of D2EHPA (di-2-ethylhexyl phosphoric acid) and TOPO (trioctyl phosphine oxide) which transfer the uranyl ion from the WPPA feed to the interior phase of the emulsion wherein said hexavalent uranium ion is reduced to tetravalent uranium ion to form a uranium-rich emulsion;

   (b) separating the uranium-rich emulsion from the WPPA feed; and

   (c) recovering the uranium from the emulsion.

2. A process according to claim 1 wherein said interior phase acid solution comprises phosphoric acid and wherein said interior phase comprises from about 15-80 volume percent of said emulsion.

3. A process according to claim 2 wherein said phosphoric acid solution in said interior phase is at a concentration of from 3-12 moles per liter.

4. A process according to either of claims 2 and 3 wherein the concentration of said phosphoric acid solution in said interior phase is substantially the same as the concentration of phosphoric acid in said WPPA solution.
5. A process according to any one of the preceding claims wherein said surfactant is a polyamine derivative of polyisobutylene succinic anhydride and has the general formula:

\[
\begin{array}{c}
\text{R}_1 \\
\text{N} \\
\text{R}_2 \\
\end{array}
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{N} \\
\text{Y} \\
\end{array}
\begin{array}{c}
\text{R}_3 \\
\text{R}_5 \\
\text{R}_7 \\
\text{R}_4 \\
\text{R}_6 \\
\end{array}
\text{x}
\]

wherein \( R_1, R_2, R_3, R_4, R_5, R_6, \) and \( R_7 \) and \( Y \) are the same or different and are hydrogen, \( C_1 \) to \( C_{20} \) alkyl, \( C_6 \) to \( C_{20} \) aryl, \( C_7 \) to \( C_{20} \) alkaryl radicals or substituted derivatives thereof; and \( x \) is an integer of from 1 to 100.

6. A process according to claim 5 wherein \( R_3 \) to \( R_7 \) are hydrogen and \( x \) varies from 3 to 20.

7. A process according to any one of the preceding claims wherein said feed/emulsion contacting is carried out in a plurality of contacting zones.

8. An emulsion process for recovering uranium from a WPPA (wet process phosphoric acid) feed which contains uranyl ions, said process comprising:

(a) contacting, in a plurality of contacting zones, said WPPA feed with a water-in-oil emulsion comprising (i) an aqueous interior phase dispersion in (ii) an oily exterior phase immiscible with both said interior phase and said feed, said interior phase comprising an acid solution containing a reducing agent and said exterior phase comprising a nonionic surfactant-containing hydrocarbon solution of D2EHPA (di-2-ethyl hexyl phosphoric acid) and TOPO (triocyl phosphine oxide) which transfer the uranyl ion from the WPPA solution to the interior phase of the emulsion wherein said uranyl ion is reduced to U(IV) ion to form a uranium-rich emulsion;

(b) separating the uranium-rich emulsion from the WPPA solution, and

(c) recovering the uranium from the emulsion; wherein excess oxidant is added to the WPPA solution.
9. A process according to claim 8 wherein said excess oxidizing agent is added to said feed prior to its contacting said emulsion.

10. A process according to claim 8 wherein said feed is sequentially contacted with said emulsion in a plurality of contacting stages or zones and said oxidizing agent is added to said feed after it has initially contacted said emulsion.

11. A process according to claim 10 wherein a portion of said excess oxidizing agent is added to said feed prior to its being contacted with said emulsion.

12. A process according to any one of claims 8 to 11 wherein said surfactant is a polyamine derivative of PIBSA.

13. A process according to any one of claims 8 to 12 wherein the concentration of the phosphoric acid in said interior phase is about the same as the concentration of phosphoric acid in the WPPA feed solution.

14. A process according to claim 13 wherein said interior phase is prepared from said WPPA feed solution.
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<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. Cl.)</th>
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The present search report has been drawn up for all claims.

Place of search: THE HAGUE
Date of completion of the search: 30-06-1982
Examiner: GRUNDEKE H.H.

CATEGORY OF CITED DOCUMENTS
X: particularly relevant if taken alone
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