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Nuclear Technology - Chemistry
and Chemical Engineering

AEC Research and Development Report

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APPLICATION OF AMIDES AS EXTRACTANTS

by

T. H. Siddall, III

Separations Chemistry Division

January 1961

[redacted]

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, South Carolina

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APPLICATION OF AMIDES AS EXTRACTANTS

by

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January 1961

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ABSTRACT

Laboratory data are given and discussed that outline the potential application of N, N-disubstituted amides to the separation of uranium, neptunium, and plutonium from fission products.

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APPLICATION OF AMIDES AS EXTRACTANTS

INTRODUCTION

A wide variety of N,N-disubstituted amides were previously reported to extract quadrivalent and hexavalent actinides strongly from nitric acid solutions.(1) The previous report emphasized theoretical and fundamental aspects of extraction by amides. The objective of the work covered in this report was to explore the process application of the amides to the recovery of uranium, neptunium, and plutonium.

SUMMARY

A preliminary investigation showed that N,N-disubstituted amides may have application as extractants for the processing of uranium, neptunium, and plutonium. These amides have potential advantages over current extractants in two types of processes in particular: sterically hindered amides are as much as ten times more selective than tributyl phosphate (TBP) for uranium and might show improved separation from fission products in such processes as the "25"(2) or Interim "23"(3) processes; unhindered amides are powerful and selective extractants for neptunium(IV) and plutonium(IV), and are comparable to anion exchange resins in this respect. These amides might be preferable to the resins simply because they are mobile liquids rather than solids, and thus could be used in existing solvent extraction equipment.

For application to the Purex process and similar processes for simultaneous recovery of uranium and plutonium, the amides have no obvious advantage other than radiation tolerance. In any process application the amides have a definite advantage over tri-n-butyl phosphate (TBP), in that the amides should tolerate a much higher radiation field. The radiation fragments from amides should be harmless in the extraction process, while the dibutyl phosphoric acid that is produced by radiolysis of TBP is very deleterious.

Several factors restrict the use of the amides in solvent extraction processes. Although the amides at moderate temperatures are about as stable hydrolytically as TBP, they would not be so stable in environments such as exist in acidic evaporators. Also, the tendency of the amides to form insoluble adducts with uranyl nitrate, and three-phase systems with nitric acids, restricts the number of amides suitable for process application. No commercial sources of these amides are known at the present time; however, there are simple and efficient syntheses so that a source could probably be developed.

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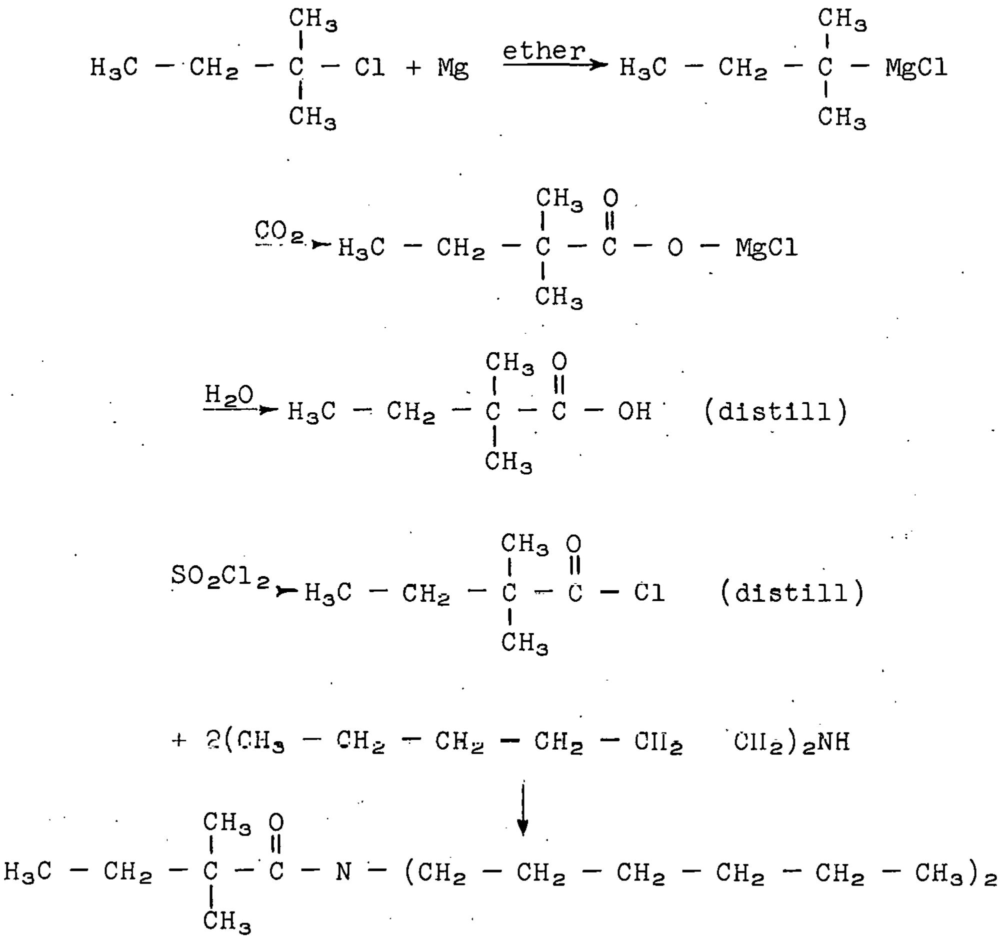
DISCUSSION

PREPARATION OF MATERIALS AND EXPERIMENTAL PROCEDURES

Most of the methods for preparation of materials and the experimental procedures have been described elsewhere$^{(1)}$. The preparations of dihexyl* dimethylethylacetamide and dihexyl methylethylisopropylacetamide are described below.

Dihexyl dimethylethylacetamide was prepared by the following sequence of reactions and operations:



$$H_3C - CH_2 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - Cl + Mg \xrightarrow{\text{ether}} H_3C - CH_2 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - MgCl \qquad (1)$$

$$\xrightarrow{CO_2} H_3C - CH_2 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - \overset{\overset{\large O}{\|}}{C} - O - MgCl \qquad (2)$$

$$\xrightarrow{H_2O} H_3C - CH_2 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - \overset{\overset{\large O}{\|}}{C} - OH \quad \text{(distill)} \qquad (3)$$

$$\xrightarrow{SO_2Cl_2} H_3C - CH_2 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - \overset{\overset{\large O}{\|}}{C} - Cl \quad \text{(distill)} \qquad (4)$$

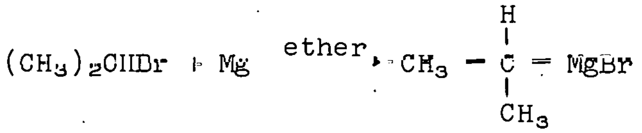
$$+ 2(CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2)_2NH$$

$$\downarrow$$

$$H_3C - CH_2 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - \overset{\overset{\large O}{\|}}{C} - N - (CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3)_2 \qquad (5)$$

(wash and distill)

The dihexyl methylethylisopropylacetamide was prepared by:



$$(CH_3)_2CHBr + Mg \xrightarrow{\text{ether}} CH_3 - \overset{\overset{\large H}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - MgBr \qquad (1)$$

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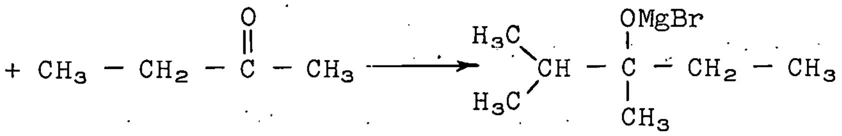
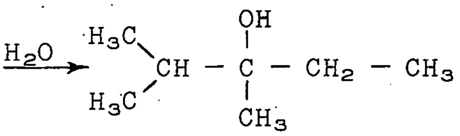
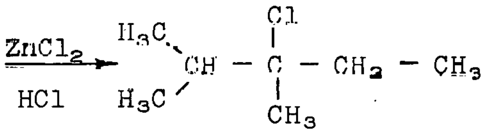
*N,N-dihexyl; in the remainder of the report N,N- is omitted to conserve space.



(2)



(distill) (3)



(distill) (4)

Continue as in step 1 with dihexyl dimethylethylacetamide. (5)

Over-all yields were small (5%), even though in the case of the methylethylisopropylacetamide the original Grignard reaction was started with three mols of isopropylbromide. This is to be expected, however, since yields for difficult steps were only 40-50%. No particular technique was needed in any step except starting the Grignard with the tertiary alkyl chlorides. These reagents have a tendency not to react at all for a while and then suddenly to react with violence. This difficulty was avoided by seeding the reaction mixture with a little preformed $CH_3 - CH_2 - MgBr$.

PHYSICAL PROPERTIES OF AMIDES

The amides of moderate molecular weight are generally colorless, mobile liquids. Cyclohexyl derivatives are an exception in that they are usually white, crystalline solids. Density data for the amides are given in the following table.

Systems of $H_2O - HNO_3$ – amide – n-dodecane have a marked tendency to form three phases. The tendency to form three phases increases with decreasing molecular weight at 30°C. The three-phase system occurs at 2M HNO_3 in the aqueous phase for 1.096M dibutylbutyramide in n-dodecane, at 4M HNO_3 for 1.096M dibutyloctanamide, and at 9M HNO_3 for 1.096M dihexyloctanamide.

Density of Amides

Amide	Density at 25°[(a)]
Dimethyloctanamide	0.92
Dimethyldecanamide	0.88
Diethyldecanamide	0.87
Dihexylformamide	0.87
Dibutylacetamide	0.90
Dibutylpropanamide	0.86
Dibutylbutyramide	0.88
Dibutylisobutyramide	0.87
Dibutyl-2-ethylhexanamide	0.86
Dibutylpivalamide	0.86
Di-sec-butylhexanamide	0.88
Dihexylacetamide	0.87

(a) All amides undiluted, but saturated with water

The solubility of the solid uranium adduct of dihexyl methylethylisopropylacetamide (I) was satisfactorily high for process application. This was not the case with dihexyl dimethylethylacetamide (II). Both amides were made up as 0.50M solutions in n-dodecane and saturated with uranyl nitrate. Compound (II) formed two liquid organic phases, which became one phase when heated to about 27°C. However, the liquid system was supersaturated because the introduction of small crystals of adduct caused precipitation of more adduct. The adduct did not dissolve completely until the sample was heated above 40°C. Compound (I) formed only a single organic phase down to 0°C. When crystals of adduct were added at 0°C a few crystals formed; however, all crystals dissolved when the temperature was raised to about 22°C.

THERMAL STABILITY

Thermal decomposition of the amides depends on structure, and occurs 20-50°C below the temperatures at which TBP decomposes. The amides also decompose more rapidly and release more heat than does TBP. Data for the thermal stability are given in the following table.

Thermal Stability of Extractants

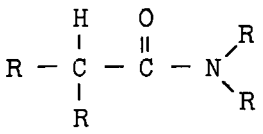
	Extractant			
	TBP	Dibutyl-butyramide	Dihexyl-octanamide	Dihexyl-pivalamide
Reaction temp., °C	197	171	164	141
Duration of temp. excursion, min	4.8	3.3	2.9	3.2
Heat of reaction				
cal/gm mixture	150	535	364	233
cal/gm HNO_3	720	1600	1590	1200
Extraction equilibrium from 10M HNO_3, mols HNO_3/mol org	1.14	1.42	1.31	0.94

While the amides are less stable then TBP, the differences in stability are not sufficiently large to cause serious complications in process applications. For example, it would be necessary to avoid introducing the amides into an acidic evaporator because a violent reaction might occur. The same precaution must be observed with TBP, and it does not appear that the more violent reaction that might occur at a somewhat lower temperature with the amide would necessitate any major change in the precautions that are presently observed with TBP.

The results in the table were obtained by differential thermal analysis. This technique consists of mixing the sample with an inert material and comparing the temperature of the mixture with that of an inert reference as both are heated from a common source. As the sample reaches the reaction temperature, a temperature excursion occurs in the sample mixture. In these experiments, all samples were equilibrated with 10M HNO_3 before testing, the sample was then mixed with ten times its weight of aluminum oxide for the thermal analysis.

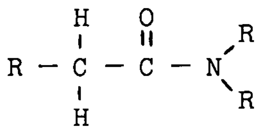
HYDROLYTIC STABILITY OF AMIDES

The hydrolytic stability of some of the disubstituted amides was about equal to that of TBP, with a marked dependence of stability on amide structure. The optimum structure for hydrolytic stability was obtained with

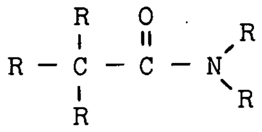


$$\mathrm{R-\overset{H}{\underset{R}{C}}-\overset{O}{\overset{\|}{C}}-N\begin{matrix}R\\R\end{matrix}}$$

For the test conditions this structure gave about twice the stability of TBP. With



the stability was about the same as with TBP and with



the amide was only about one-fifth as stable as TBP.

Both 1-hexanoylpiperidine and n-butylphenyl n-butyramide showed outstandingly high apparent rates of hydrolysis. In both cases there was visible evidence of general destruction, and both compounds probably underwent nitration or other side reactions that may qualify the hydrolytic results. The phenyl group in n-butylphenyl n-butyramide may also have been nitrated; however, it is interesting to note that the phenyl group in dibutylbenzamide did not lead to unusual instability or side reactions. Data for the hydrolysis of TBP and the amides are given in the table.

Hydrolysis of Undiluted Disubstituted Amides

Compounds	% Hydrolysis(a)
Dibutylbutyramide	0.40
Dibutylhexanamide	0.51
Di-2-butylhexanamide	0.59
Dibutylisobutyramide	0.27
Dibutylcyclohexanecarboxamide	0.31
Dibutyl-2-ethylhexanamide	0.25
Dibutylpivalamide	2.4
1-Hexanoylpiperidine	30(b)
N-Butyl-N-phenylbutyramide	7(b)
Dibutylbenzamide	0.61
TBP	0.5

(a) Heated for 67 hours at 70°C

(b) Samples badly discolored after exposure

The data for the amides were obtained by holding samples of pure amides at 70°C in an oil bath for 67 hours. The samples were equilibrated with 3.0M nitric acid and separated from the aqueous phase before being placed in the bath. The degree of hydrolysis was determined by titrating the carboxylic acid in the organic phase after washing out nitric acid with water. The data for TBP were extrapolated from earlier work.(4)

EQUILIBRIUM DISTRIBUTION DATA

Equilibrium distribution data are given in the table. Reference (1) should be consulted for additional distribution data. Most of the data in reference (1) are for 0.50M amide in toluene as a diluent; however, for purposes of comparison between amides, and for observing trends, these data should serve as well as those obtained with an aliphatic diluent.

Extraction(a) by Disubstituted Amides

Extraction by 1.09M Dibutyloctanamide in n-Dodecane at 30°C(b)

E_{HNO_3}	E_U	$E_{Pu(III)}$	$E_{Np(IV)}$	E_{Th}	E_{Zr}
0.069(0.49)(c)	0.55(0.49)	0.33(0.62)	0.172(1.24)	0.017(1.24)	0.015(1.39)
0.119(0.97)	1.80(0.97)	1.12(1.03)	3.11(2.45)	0.33(2.45)	0.028(2.66)
0.186(1.74)	5.6(1.74)	6.6(1.88)	9.6(3.12)	0.80(3.12)	0.039(3.33)
0.222(2.66)	10.7(2.66)	32.6(2.83)	21.9(3.80)	2.37(3.80)	0.070(3.94)
0.226(3.32)	14.0(3.32)	74(3.50)			0.096(4.56)
0.197(4.61)	19.5(4.61)	187(4.92)			0.125(4.71)

Extraction by 1.09M Dihexyloctanamide in n-Dodecane at 30°C

$E_{Np(IV)}$	E_{Th}	E_{Zr}
0.67(1.60)	0.025(1.63)	0.21(5.9)
1.19(2.00)	0.057(2.09)	
19.3(4.80)	1.83(4.92)	

Extraction by 100% Dimethyldecanamide at 30°C

E_{Pm}	E_{Am}	E_{HNO_3}	E_{Zr}	$E_{Np(IV)}$	E_{Th}	E_U
0.056(4.45)	0.063(10.2)	1.19(0.85)	0.31(0.85)	0.26(0.020)	28(3.0)	39(3.0)
0.037(8.1)	0.128(13.0)	1.01(2.71)	1.0(2.71)	1.46(0.17)	64(6.0)	25(6.0)
0.086(11.5)		0.96(3.64)	1.5(3.64)	8.7(0.53)		
0.137(12.7)		0.83(5.5)	2.6(5.5)	22.5(1.17)		
		0.77(7.2)	2.3(7.2)	123(2.00)		
		0.75(8.2)	2.1(8.2)	156(2.43)		
				320(3.00)		
				> 1000(6.0)		

(a) E is the symbol for extraction coefficient.

(b) Three-phase system at and above 4.95M HNO_3 in the aqueous phase at 30°C.

(c) Concentration of nitric acid in the aqueous phase is given in parentheses immediately after the value of the extraction coefficient.

Extraction of uranyl nitrate and of nitric acid by the amides is qualitatively, and to some degree even quantitatively, similar to that by TBP and related compounds. The extraction of quadrivalent actinides is qualitatively different in that extraction at high acidity is higher relative to that at low acidity. The extraction of zirconium nitrate by the amides is very different. Extraction of zirconium maximizes at about 6M nitric acid in the aqueous phase. With organophosphorus compounds the extraction of zirconium is a monotone that reaches very high values at high acidity.

TEST WITH PUREX FEED

In batch equilibration tests that simulated the 1A bank of the Purex process, dihexyloctanamide was superior to TBP for gross gamma and zirconium-niobium decontamination. However, the amide was slightly inferior in terms of ruthenium decontamination. The two extractants as 1.09M solutions in n-dodecane were compared in parallel experiments in which the feed stage was simulated with adjusted raw metal solution from the Purex process. After contact with the raw metal solution, each extractant was scrubbed three times with an equal volume of 0.2M $UO_2(NO_3)_2$ in 3M HNO_3. After this treatment samples of the two extractants contained the activities shown in the table below.

Comparison of Extractants

Extractant	Total γ, c/m/ml	Zr-Nb γ, c/m/ml	Ru γ, c/m/ml
TBP	$4.6x10^4$	$4.5x10^4$	$2x10^3$
Dihexyloctanamide	$8x10^3$	$3x10^3$	$5x10^3$

PROCESS IMPLICATIONS

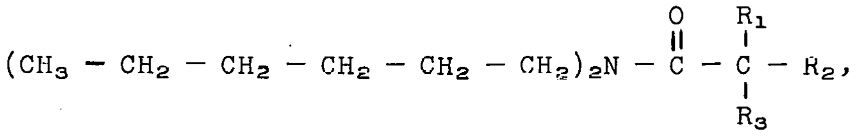
The N,N-disubstituted amides have potential advantages over already accepted reagents in two types of processes. The first type of process would be for the recovery of quadrivalent actinides. Undiluted amides with straight chains are very powerful and selective extractants for quadrivalent actinides and are very similar to anion exchange resins in this respect. They might be superior replacements for anion exchange resins, primarily because they are mobile liquids of low density. They would be applicable to batch contacts or to multistage operation. Existing solvent extraction contactors, washers, and other equipment presumably could be utilized without major modification. No special waste disposal problem would be anticipated because hydrolytic or radiolytic products could be easily washed away by conventional techniques, and the residual amide retained in a purified condition.

A shortcoming common to most of the amides is the tendency to form solid adducts with uranyl nitrate; these adducts have a low solubility in either excess amide or in aliphatic diluents. In some cases there is also a tendency for solutions of amides in paraffins to form a three-phase system with even moderate concentrations of nitric acid. Only a limited number of structural types are free of these difficulties.

As a consequence, if the quadrivalent actinides are to be recovered in the presence of uranium, dihexyloctanamide or some other amide of similar molecular weight must be employed. Because of its high molecular weight the dihexyloctanamide is more viscous than dimethyl or diethyl derivatives. Dilution might be required in order to obtain a satisfactory viscosity for contactor operation. Unfortunately the extraction of quadrivalent actinides is highly dependent on amide concentration(1). For example a drop of about a factor of ten in extraction would be encountered if 100% amide were diluted with an equal volume of n-dodecane.

For these reasons it is not certain that a single-batch extraction with an amide could give sufficient neptunium recovery from the Purex wastes. It might be necessary to use a dilution of dihexyloctanamide that would give an extraction coefficient of about 100 for neptunium(IV). In this case several batch contactors in series would be required for high recovery.

The second type of process in which amides might be used to advantage is represented by the "25" and Interim "23" processes, or whenever uranium is to be recovered without simultaneous recovery of quadrivalent actinides. Certain highly branched amides, the dihexyltrialkylacetamides



$$(CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2)_2N - \overset{\overset{O}{\|}}{C} - \underset{\underset{R_3}{|}}{\overset{\overset{R_1}{|}}{C}} - R_2,$$

exhibit a very high order of selectivity for uranium(1) and should give a separation from fission products superior to that obtained with TBP.

For uranium recovery with highly branched amides the uranyl nitrate adducts of the lower homologues such as dihexylpivalamide are too high melting and too insoluble for these homologues to have process application. Apparently the carboxylic acid intermediate must contain at least seven carbon atoms. This makes the supply of a satisfactory amide dependent on intermediates that are still undergoing commercial development(5).

For general use in solvent extraction in high radiation fields or other drastic conditions the amides have an outstanding advantage over TBP and all similar compounds. The primary radiolytic and hydrolytic fragments from the amides should be amines and carboxylic acids. Rather large amounts of these fragments should be tolerable without serious interference to the use of the amides. There should be no deleterious fragments of the amount and quality of the DBP that arises from TBP. In that sense the amides should have a very high tolerance to radiation, even though they prove not to be more radiation resistant.

It should be pointed out that no tests of radiation stability of amides were made in the course of this work. However, unless unexpectedly high instability is encountered, no adverse effect is anticipated from radiation damage except consumption of reagent.

Aside from consideration of viscosity there is another practical limitation on allowable molecular weight for amide molecules. Amine fragments larger than dihexylamine, and acid fragments larger than decanoic acid, cannot be readily removed from the amides or solutions of amides by simple washing techniques. The higher amines are too soluble in the organic phase and the higher acids form soaps with caustic washes. Even with decanoic acid, considerable technique was required to remove excess acid from laboratory preparations of decanamides. If heavier amides were used in process application, some solvent recovery treatment such as distillation at very low pressure would be required rather than simple basic and acidic washes.

The amides do not especially recommend themselves for use in processes for the simultaneous recovery of hexavalent and quadrivalent actinides such as the Purex process. Highly branched amides cannot be used to improve selectivity for uranium, because at the same time the extraction of quadrivalent actinides would be markedly decreased. The one test with dihexyloctanamide indicates that the straight-chain compounds have no significant advantage over TBP in terms of decontamination. The only obvious advantage of the amides lies in the probable high tolerance to radiation. This might be a decisive advantage in recovery of breeder fuels in which very high radiation is to be expected.

Finally, within the author's knowledge, commercial supplies of suitable amides are not available. If large-scale application were anticipated, a source of supply would have to be developed. Since there are several simple and efficient syntheses, this should not be a problem.

SUGGESTIONS FOR FUTURE WORK

While at the present time there seems to be no urgency to replace TBP or anion exchange resins by better process reagents, it is desirable to complete the testing of amides for process application within a reasonable time. An improvement in present processes might be obtained, but, more important, a technique might be developed and placed in reserve against processing requirements of the future. An extractant with high radiation tolerance may be important for processing some of the power fuels. For example the processing of fuel from such reactors as the Fast Oxide

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Breeder(6) definitely extends the process capabilities of TBP to the limit.

The following experiments are suggested:

1. Miniature mixer-settler runs with full-level "25" process feed and a suitable dihexyltrialkylacetamide. These runs should be made even if no commercial supply of amide or intermediates is in prospect.

2. Batch contactor operations with dihexyloctanamide to recover neptunium and/or plutonium from actual 1AW concentrate.

3. Miniature mixer-settler runs with dihexyloctanamide for the simultaneous recovery of uranium and plutonium with radiation exposures of up to 100 watt-hours per liter of solvent per pass.

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BIBLIOGRAPHY

1. Siddall, T. H., III, "Effects of Structure of N,N-Disubstituted Amides on Their Extraction of Actinide and Zirconium Nitrates and of Nitric Acid." J. Phys. Chem. 65, (January 1961).

2. Parker, S. G., W. E. Prout, and T. H. Siddall, III. Solvent Extraction of Enriched Uranium. E. I. du Pont de Nemours & Co. Savannah River Laboratory, Aiken, S. C. AEC Research and Development Report DP-122, 3 pp. (June 1955)(Secret).

3. Hylton, C. D. Separation of U^{233} in the ORNL Pilot Plant. Oak Ridge National Lab., Tenn. AEC Research and Development Report ORNL-1425, 36 pp. (December 1952)(Secret).

4. Dukes, E. K. The Formation and Effects of Dibutyl Phosphate in Solvent Extraction. E. I. du Pont de Nemours & Co. Savannah River Laboratory, Aiken, S. C. AEC Research & Development Report DP-250, 22 pp. (November 1957).

5. Neo-Heptanoic Acid, MD-237 (New Products Data Sheet) Market Development Division, Enjay Company, Inc., January 1960.

6. Jones, S. S. The Fast Oxide Breeder - Radiation Effects in Chemical Processing of Fast Oxide Breeder Fuel. General Electric Co. Knolls Atomic Power Laboratory, Schenectady, N. Y. AEC Research and Development Report KAPL-1758, 38 pp. (June 1957).

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