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AEC RESEARCH AND DEVELOPMENT REPORT

## STUDIES OF TRAMEX SOLVENT

### I. EFFECTS OF MAJOR IMPURITIES IN TERTIARY AMINE EXTRACTANTS

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# STUDIES OF TRAMEX SOLVENT

## I. EFFECTS OF MAJOR IMPURITIES IN TERTIARY AMINE EXTRACTANTS

by

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#### ABSTRACT

Secondary amines were found to be the major impurities in commercial lots of three tertiary amines: "Alamine" 336, "Alamine" 336-S, and "Adogen" 364. These impurities form precipitates or emulsions when the tertiary amines are used as the extractant for americium and curium in the Tramex process. Tentative purchase specifications for Tramex extractant are proposed.

## CONTENTS

	<u>Page</u>
Introduction . . . . .	5
Summary . . . . .	5
Discussion . . . . .	6
Commercial Tertiary Amine Extractants . . . . .	6
Primary and Secondary Amine Impurities . . . . .	7
Other Impurities . . . . .	8
Precipitate Formation on Amine Contact with LiCl-HCl. . . . .	8
Specifications . . . . .	10
Bibliography . . . . .	12

## List of Tables

### Table

I	Manufacturers' Specifications for Tertiary Amine Extractants . . . . .	6
II	Observations and Comparisons of Extractants . . . . .	9

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## I. EFFECTS OF MAJOR IMPURITIES IN TERTIARY AMINE EXTRACTANTS

### INTRODUCTION

A tertiary amine extractant is used in the Tramex process for the separation of americium and curium from lanthanides and fission products.<sup>(1)</sup> In laboratory-scale demonstrations of the process with nonradioactive synthetic feeds, problems arose when highly stable emulsions were formed or when voluminous precipitates appeared in the solvent phase. This adverse behavior was attributed to impurities in the extractant, and a program was initiated to identify and characterize the behavior of these impurities.

This report describes the determination of the major impurities in commercial lots of "Alamine" 336,\* "Alamine" 336-S, and "Adogen" 364\*\* and recommends specifications for the purchase of amine extractants for use in the process.

### SUMMARY

Secondary amines were the principal impurities in commercial lots of "Alamine" 336, "Alamine" 336-S, and "Adogen" 364. Conditions were defined under which these impurities tended to precipitate or form emulsions. Other impurities were shown to be present but were not identified.

Tentative specifications for the purchase of Tramex extractants were established.

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\* "Alamine" is a trademark of General Mills.

\*\* "Adogen" is a trademark of Archer Daniels Midland Company for fatty nitrogen compounds.

## DISCUSSION

### COMMERCIAL TERTIARY AMINE EXTRACTANTS

Three commercially available tertiary amines, "Alamine" 336 (technical grade), "Alamine" 336-S (reagent grade), and "Adogen" 364, were investigated during May 1963—February 1964. The manufacturers' specifications for these products are listed in Table I. Since the time of this work, both manufacturers of the amines have expressed willingness to supply fatty tertiary amines of exceptionally high purity.

TABLE I

Manufacturers' Specifications for Tertiary Amine Extractants

	<u>"Alamine" 336</u>	<u>"Alamine" 336-S</u>	<u>"Adogen" 364</u>
Alkyl-chain length distribution	C <sub>8</sub> -C <sub>10</sub> mixture with the C <sub>8</sub> predominating	C <sub>8</sub> -C <sub>10</sub> mixture with the C <sub>8</sub> predominating	5% C <sub>8</sub> 60% C <sub>9</sub> 33% C <sub>10</sub> 2% C <sub>12</sub>
Amine value <sup>(a)</sup>	134	(b)	141
Tertiary-amine content, %			
Minimum	90	99	95
Typical	95		97
Secondary-amine content, %			
Maximum	4	(b)	4
Typical	1.5		1.4
Primary-amine content, %			
Maximum	2	(b)	2
Typical	-		-
Water content, %			
Maximum	0.5	(b)	0.5
Typical	0		0.1

(a) KOH equivalent: mg KOH per g amine.

(b) Not stated, but should be at least as good as "Alamine" 336

Early analytical work was concerned with the identification of deleterious impurities in "Alamine" 336 and "Alamine" 336-S. However, after available commercial lots of "Adogen" 364 performed more efficiently under Tramex process conditions than available commercial lots of "Alamine" 336 and "Alamine" 336-S, subsequent analytical work was centered on "Adogen" 364. Consequently, evaluation of "Alamine" 336 was discontinued before definitive data were obtained, and certain phases of the work on "Alamine" 336-S were not completed.

## PRIMARY AND SECONDARY AMINE IMPURITIES

The most probable impurity in a tertiary amine is secondary amine. Of several known methods for the determination of secondary (and/or primary) amines, the near-infrared spectrophotometric method of Lohman and Norteman<sup>(2)</sup> was chosen. Though the limit of detection is relatively high (0.3 wt % as dioctylamine), the method was adopted because of its simplicity and speed. Reference standards of tertiary amines were obtained by acetylating "Adogen" 364 with acetic anhydride to convert the secondary and primary amines to the corresponding acetamides, *which* do not contribute to the analytical absorption band. "Adogen" 364 and "Alamine" 336-S each contained about 2 wt % secondary amine (as dioctylamine). "Alamine" 336-S contained only 1.0 wt % secondary amine after being passed through a charcoal column. No primary amines were detected, but the detection limit for primary amines was 0.2 wt % (as octylamine).

Poor phase separation resulted when diethylbenzene (DEB) solutions of primary and secondary octylamines were contacted with solutions of 11M LiCl-0.02N HCl. When 1 wt % dioctylamine in DEB was contacted with the LiCl solution, phase separation was quite slow and some solids were produced in the organic phase and settled at the interface. In contrast to the behavior of dioctylamine, mono-octylamine at concentrations of ~0.7 wt % in DEB produced some foaming, and although disengagement was fairly rapid, the aqueous phase remained turbid. At higher concentrations of mono-octylamine, the aqueous phase formed a solid gel.

Passage of free "Alamine" 336 through a coconut-charcoal filter removed the pale yellow coloration from the amine and produced an extractant that performed satisfactorily in subsequent mixer-settler process studies. This charcoal-treated material produced no precipitate upon contact with 11M LiCl-0.02N HCl either as the free amine or as the amine hydrochloride. Analysis of a chloroform eluate from the charcoal indicated that the charcoal column had reduced the concentration of secondary amine. The yellow component was eluted also, but it was not separated from the residual tertiary amine with which it was co-sorbed on the charcoal.

The samples of "Alamine" 336-S and "Adogen" 364 that were contacted with 11M LiCl-0.02N HCl gave almost equal amounts of precipitate, but in subsequent process development tests in the mixer-settlers, "Adogen" 364 performed better than "Alamine" 336-S. "Alamine" 336 gave significantly greater amounts of precipitate and performed poorly in the process tests. Samples that were first charcoal treated produced little or no precipitate and performed adequately in process tests.

Repeated contact with 11M LiCl-0.02N HCl depleted the deleterious species from each of the extractants that were tested. Depletion of



the precipitate-forming species did not remove the yellow coloration from the extractant. From this it was concluded that the coloration was not deleterious to the process.

#### OTHER IMPURITIES

"Alamine" 336 and "Alamine" 336-S contained a reducible species detectable by polarographic methods at +1.8 volts vs. a standard calomel electrode. Charcoal treatment removed the species. "Adogen" 364 did not contain such a species. The reduction wave did not result from amine oxides or lower amines, but this species was not identified further.

Impurities that might be deleterious could arise from the production process for the tertiary amine. Such impurities were not detected in "Alamine" 336, "Alamine" 336-S, and "Adogen" 364, but were detected in "Adogen" 363, a tertiary amine differing from "Adogen" 364 only in that its alkyl-chain distribution is  $C_{12}$ -centered instead of  $C_8$ -centered (Table I above). "Adogen" 363 precipitated solids when maintained at 20°C. When these solids were washed with cold hexane, a white powder remained. The X-ray diffraction pattern of the powder approximated that of typical glycerides. Hydrolysis of the powder with sodium hydroxide yielded a solid, whose infrared spectrum was typical of a long-chain carboxylic acid salt. Acidification of this salt produced a solid, whose infrared spectrum was that of a carboxylic acid. It was concluded that certain fatty-acid starting materials were carried through the process unreacted or that crosscontamination had occurred during manufacture or packaging.

One lot of "Adogen" 364 contained a voluminous solid, which was removed by centrifugation before the extractant was used in the process. The removed solid was filtered free of excess tertiary amine and washed with cold hexane. X-ray diffraction data indicated a crystal structure similar to that of refined paraffin wax. The melting point was 70°C. The gray coloration of the material indicated a possible mixture. The major fraction (~80%) of the solid was soluble in chloroform, and the insoluble residue was olive brown and apparently inorganic. Evaporation of the chloroform produced a white solid. Neither solid was identified.

#### PRECIPITATE FORMATION ON AMINE CONTACT WITH LiCl-HCL

All precipitates were obtained by contacting the free amines in hexane with 11M LiCl-0.02N HCl, since considerably larger quantities of precipitate were formed when tests were made with free amines instead of amine hydrochlorides, and with hexane diluent instead of DEB. The

precipitates were washed with hexane and water without appreciable losses. Data on the precipitates formed from various extractants are summarized in Table II.

TABLE II  
Observations and Comparisons of Extractants

	<u>"Alamine" 336-S</u>		<u>"Adogen" 364</u>
	<u>Untreated</u>	<u>Charcoal-Treated</u>	<u>Untreated</u>
LiCl precipitate <sup>(a)</sup>	copious	none	moderate
LiCl precipitate <sup>(b)</sup>	moderate	none	very light
LiCl precipitate <sup>(c)</sup>	very light	none	none
Secondary amine, % <sup>(d)</sup>	~2	~1	~2
Reducible species	polarographic wave at -1.8 v vs. S.C.E.	no wave	no wave

- (a) Formed when free amine undiluted or with hexane diluent was contacted with 11M LiCl-0.02N HCl.  
 (b) Formed when 0.6M free amine in DEB was contacted with 11M LiCl-0.02N HCl.  
 (c) Formed when 0.6M amine hydrochloride in DEB was contacted with 11M LiCl-0.02N HCl.  
 (d) By near-infrared spectrophotometric method of Lohman and Norteman. <sup>(2)</sup>

The precipitate from "Adogen" 364 was mainly dioctylamine hydrochloride, but the precipitate from "Alamine" 336-S was identified as a mixture of secondary amine hydrochlorides with an alkyl-chain distribution different from that of "Adogen" 364. Dilute hydrochloric acid was solely responsible for the precipitation. The "Adogen" 364 precipitate was similar to dioctylamine hydrochloride with respect to color (pink), melting point (205-220°C), crystal structure (X-ray diffraction), infrared spectra, and reactivity with various reagents such as concentrated H<sub>2</sub>SO<sub>4</sub>. The "Alamine" 336-S precipitate compared similarly except that its color was off-white and it was more gelatinous.

A precipitate that formed when 11M LiCl-0.02N HCl contacted a process solution of 30 vol % "Alamine" 336 hydrochloride in DEB was not identified. However, it is unlikely that this precipitate was entirely secondary amine hydrochloride in view of the solubility of dioctylamine hydrochloride in solutions of tertiary amine hydrochlorides in DEB.

Before the precipitates were identified, they were thought to be carbamates, because upon exposure to air primary and secondary amines were observed to form solids that were identified as ammonium carbamates. Such carbamate salts evolve carbon dioxide when treated with sulfuric acid. However, when gas evolved from the precipitates was analyzed by mass spectrometry, carbon dioxide was found to be a minor constituent in comparison with hydrogen chloride. Though the presence of significant quantities of carbamate may be rejected, small quantities may be present, and if the primary-amine contents of the extractants are not kept quite low, trouble from carbamate formation might arise.

#### SPECIFICATIONS

There are a number of potential impurities in tertiary amine extractants that could cause emulsification or precipitation problems in the Tramex process if present in sufficient quantities. Secondary amines are quite troublesome because their acid salts can precipitate when the extractant is contacted with acidic lithium chloride solutions. The solubility of the acid salts in DEB apparently varies with the alkyl-chain length of the secondary amine impurity. Although "Adogen" 364 with 2 wt % secondary amine has performed adequately in the process, a secondary amine specification of 1 wt % maximum would be desirable in view of the fact that alkyl-chain length distributions might vary. Primary amines, although not likely to be present to any great extent in the extractants, cause poor phase disengagement. No detectable amounts (~0.2 wt % by near-infrared method) should be present. Other impurities, e.g. the reducible species present in "Alamine" 336-S, in the starting materials and in the manufacturing intermediates must be excluded.

It is impossible to predict all impurities that could be present in tertiary amine extractants, and some variations in purity have been observed from lot to lot of the same extractant. To provide guidelines for the purchase of a satisfactory extractant from any commercial source, the following tentative specifications are recommended:

1. Tertiary amine content: 99 wt % or greater
2. Secondary amine content: 1 wt % or less
3. Primary amine content: 0.2 wt % or less
4. Particulate solids: absent

5. Alkyl-chain length distribution: greater than 90% in  $C_8$ - $C_{10}$  range; no components with chain lengths greater than  $C_{12}$ , nor less than  $C_6$ .
6. Starting materials or production intermediates, e.g., glycerides, amines, and alcohols: absent
7. Polarographically reducible species (especially those giving a wave at -1.8 volts vs. S.C.E.): absent
8. Use test (must pass satisfactorily):
  - a. Make a solution of 30 vol % extractant in diethylbenzene.
  - b. Neutralize extractant by contacting solvent with an equal volume of 1M HCl.
  - c. Remove aqueous phase and contact neutralized solvent with an equal volume of 0.01M HCl. The contact with 0.01M HCl will remove excess hydrogen chloride from the solvent.
  - d. Remove aqueous phase and contact organic phase with an equal volume of 11M LiCl-0.02M HCl.

No precipitates should form and the phases should disengage cleanly within 5 minutes. Disengaging time is highly dependent upon the hydrochloric acid concentration in the aqueous lithium chloride solution.

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