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AEC Research and Development Report

COMPOSITION AND STABILITY OF "ULTRASENE"

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D. L. West

Analytical Chemistry Division

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

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ABSTRACT

"Ultrasene"* typically contained 57 wt % branched paraffins and cycloparaffins, 40 wt % n-paraffins, 3 wt % aromatics, and less than 0.1 wt % olefins. The n-paraffinic fraction from "Ultrasene" was stable to chemical and radiolytic degradation, whereas the combined branched paraffinic and cycloparaffinic fraction, and the aromatic fraction, were significantly less stable.

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* Product of the Atlantic Refining Co.

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COMPOSITION AND STABILITY OF "ULTRASENE"

INTRODUCTION

The Purex process is a solvent extraction process that is employed to separate and recover plutonium and uranium from the fission products. Tri-n-butyl phosphate (TBP), diluted with a hydrocarbon diluent, is the usual Purex solvent. "Ultrasene"*, a purified kerosene, is a diluent employed at the Savannah River Plant. Radiolytic and chemical degradation of the solvent complicate and limit the efficiency of the Purex process. During the extraction process, both the extractant, TBP, and the diluent, "Ultrasene", degrade to form small quantities of troublesome ligands that complex zirconium and other undesirable fission products.(1) The principal zirconium ligand produced from TBP is di-n-butyl phosphate (DBP), which may be removed from degraded solvent by a caustic wash. However, some of the ligands produced from the degradation of "Ultrasene" are not removed by either caustic or acid washes.(2,3)

The ligands carry zirconium with the plutonium and uranium as they are extracted into the solvent phase in the Purex process. Some of the extracted zirconium is stripped with the plutonium and uranium in the second and third contactors, respectively, and a substantial amount of zirconium remains with the spent solvent from the first cycle of solvent extraction. The zirconium that is extracted into the plutonium and uranium product streams causes poor product quality. The buildup of zirconium in the stripped solvent complicates the washing of the solvent and the maintenance of the solvent handling system.

This report describes the work that was done to determine the compounds and classes of compounds in "Ultrasene" that degrade to form zirconium ligands.

SUMMARY

Compositional analyses showed that "Ultrasene" is composed principally of normal, highly branched, and cyclic paraffins in the C_{11} to C_{16} range. A typical composition for "Ultrasene" was 57 wt % branched and cyclic paraffins, 40 wt % n-paraffins, 3 wt % aromatics, and less than 0.1 wt % olefins. Gas chromatography, infrared spectrophotometry, and low ionizing voltage mass spectrometry were employed in the compositional analyses.

The n-paraffins in "Ultrasene" were stable to both radiolytic and chemical degradation, whereas the nonlinear components were unstable. The tendency of the normal paraffins in "Ultrasene" to form zirconium ligands was approximately the same as for n-dodecane, which was employed as a standard for stability. The aromatic components degraded to form relatively large amounts of zirconium ligands. However, the stability

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*Product of the Atlantic Refining Co.

of aromatic-free "Ultrasene" was not improved over that of virgin "Ultrasene".

The data indicated that the principal precursors of zirconium ligands in "Ultrasene" are highly branched paraffins or cycloparaffins containing 11 to 16 carbon atoms. On the basis of this study a Purex diluent containing only normal paraffins of 11 to 16 carbon atoms was recommended.

DISCUSSION

EXPERIMENTAL METHODS

Since "Ultrasene" is a refined kerosene and probably contains thousands of compounds, a simplified approach was selected for isolating the precursors of zirconium ligands. "Ultrasene" was first fractionated according to compound class, then the composition and stability of each type were studied. The separation scheme, shown in Figure 1, was chosen because it could be employed with reasonably large samples (500 ml) and relatively simple equipment. In this scheme, the "Ultrasene" was first treated with urea according to the method of Zimmerschied(4) to separate the linear components from the nonlinear components. The nonlinear components were then separated into aromatic and nonaromatic fractions by liquid-solid chromatography on silica gel.(5) Finally the nonaromatic, nonlinear components were separated into a highly branched paraffinic and cycloparaffinic fraction and a slightly branched paraffinic fraction by treatment with thiourea.(6)

Compositional analyses and stability tests were performed on each of the fractions. Gas chromatography, infrared spectrophotometry, ultraviolet spectrophotometry, and low ionizing voltage mass spectrometry (LIVMS)(7) were employed in the determination of the composition of the fractions. The radiolytic and chemical stabilities* of each fraction were determined by degrading 30% TBP solvents made from the fractions and measuring the concentration of zirconium ligands in the degraded solvents with the "Z Test".(8) Although this test was designed to determine the stability of the diluent, TBP was added to more closely simulate process conditions and to extract more acid into the organic phase during degradation. A detailed description of the degradation conditions and postdegradation treatments is given in the Appendix.

Two different lots of "Ultrasene" were analyzed in this study. Lot 1 was delivered in a tank car from the Atlantic Refining Co. in February 1960, and was the Purex diluent employed in the Plant at the time of this study. Lot 2 was purchased from the same source, probably in a 50-gallon drum, in early 1959. Because Lot 1 was the current

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* In this report "stability" means the resistance of the diluent to degradation, under the conditions defined in the Appendix, to form ligands that complex zirconium.

diluent, it was taken as typical of "Ultrasene". Only the aromatic contents of the two lots differed significantly, and the difference is discussed in more detail under "Stability of Components in 'Ultrasene'".

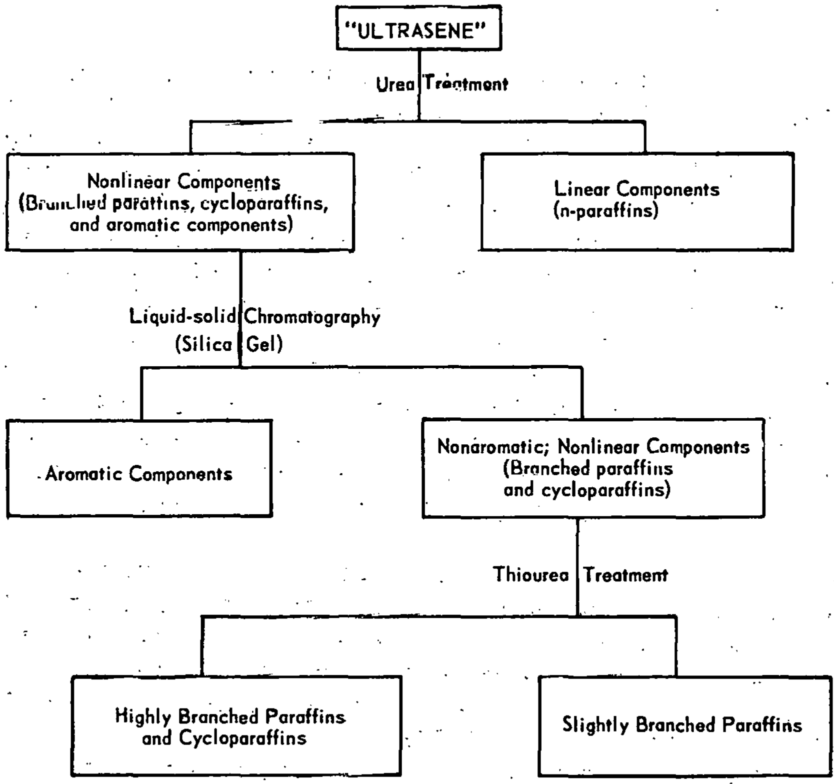


FIG. 1 SEPARATION SCHEME FOR "ULTRASENE"

COMPOSITION OF "ULTRASENE"

Compositional analyses showed that "Ultrasene" is composed principally of normal, branched, and cyclic paraffins with small amounts of aromatics and essentially no olefins. A typical compositional analysis of "Ultrasene" is given in Table I.

TABLE I

Typical Composition of "Ultrasene"

Component	Concentration, wt %	
n-Paraffins		40
n-Nonane and lower	<0.2	
n-Decane	1	
n-Undecane	4	
n-Dodecane	14	
n-Tridecane	16	
n-Tetradecane	4	
n-Pentadecane	1	
n-Hexadecane and above	<1	
Branched paraffins, cycloparaffins, and polycycloparaffins		57
Aromatic Compounds		3
Alkyl benzenes	1.8	
Aromatic-cycloparaffins (mixed type)	1.1	
Alkyl indenes	0.02	
Alkyl naphthalenes	0.1	
Other aromatic compounds	<0.01	
Olefins		<0.1

Gas chromatographic analyses of the fractions from the urea treatment of "Ultrasene" provided a reasonably complete analysis for the n-paraffins but the branched and cyclic paraffins were not sufficiently resolved by the gas chromatograph to permit identification and analysis. Separation of "Ultrasene" into linear and nonlinear fractions with urea gave the yields shown in Table II. Gas chromatographic analysis of these two fractions, Figure 2, showed that the linear fraction was essentially a mixture of pure n-paraffins and the nonlinear fraction contained about 15 wt % of the n-paraffins. The data given in Table I for the n-paraffins were computed from the gas chromatographic analyses of the fractions from this urea separation.

TABLE II

Yields from Urea Treatment of "Ultrasene"

Fraction	Yield, wt % of Starting Material
Nonlinear components	55
Linear components	30
Total yield	85
Loss	15
Total	100

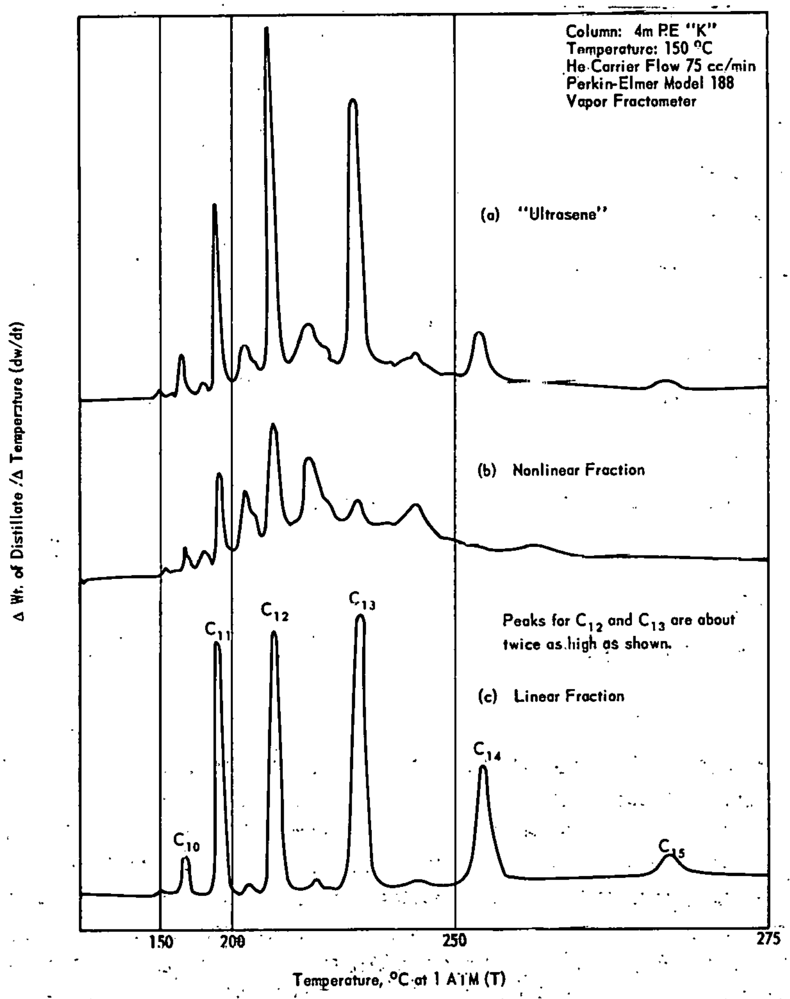


FIG. 2 CHROMATOGRAMS OF "ULTRASENE" FRACTIONS

The gas chromatograms of Figure 2 are presented as differential distillation curves to provide additional information concerning the composition of the sample. To obtain this curve, the chromatograph was calibrated for the boiling point of hydrocarbons so that the time scale on the conventional chromatogram became a measure of the boiling points at one atmosphere. Since the detector of the chromatograph was a differential thermal conductivity cell, the response was equivalent to the change in weight of eluted material with a change in time (or, with calibration, a change in boiling point). Thus after calibration, the conventional chromatogram was utilized as the differential of an analytical distillation curve and thereby provided information on the boiling points of the components in the sample.

Analysis by LIVMS of the fractions from a liquid-solid chromatographic separation of Lot 1 "Ultrasene" on a silica gel column revealed at least 19 different aromatic compounds and 12 different cycloparaffins. The LIVMS work is described in detail in another report.(7) A list of the aromatic compounds that were observed is shown in Table III. The LIVMS data were employed to estimate the typical concentrations of aromatic compounds shown in Table I. The 12 cycloparaffins observed in "Ultrasene" by LIVMS analyses are shown in Table IV.

TABLE III

Types of Aromatic Compounds Observed in "Ultrasene"

Alkyl benzenes	C_nH_{2n-6}	C_{11} through C_{14}
Aromatic-cycloparaffins (mixed type)	C_nH_{2n-8}	C_{11} through C_{14}
Alkyl indenes	C_nH_{2n-10}	C_{11} through C_{14}
Alkyl naphthalenes	C_nH_{2n-12}	C_{11} through C_{13}
Other aromatic compounds	C_nH_{2n-14}	C_{12} through C_{14}

TABLE IV

Types of Cycloparaffins Observed in "Ultrasene"

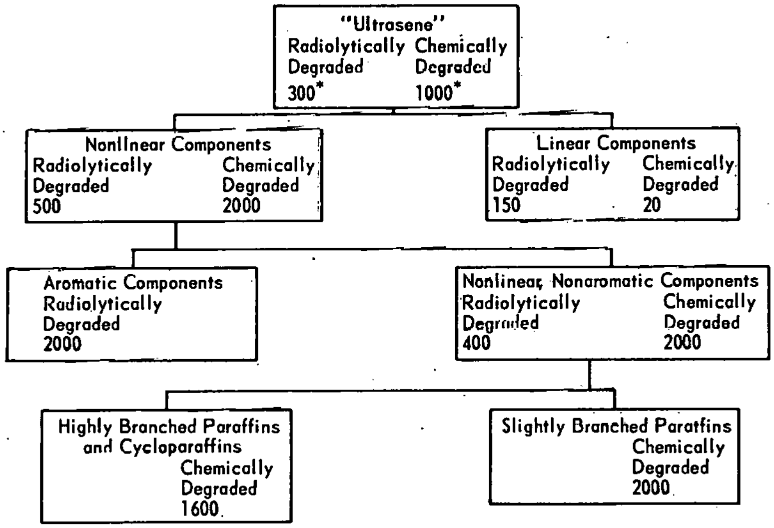
Monocycloparaffins	C_nH_{2n}	C_{11} through C_{14}
Dicycloparaffins	C_nH_{2n-n}	C_{11} through C_{14}
Tricycloparaffins	C_nH_{2n-4}	C_{11} through C_{14}

The olefin content of "Ultrasene" was determined from the "bromine number"(9) and from infrared analyses of the eluates from the silica gel chromatography of "Ultrasene". A "bromine number" of 0.08 with a standard deviation of 0.04 indicated that the olefin content of "Ultrasene" was less than 0.1 wt %. Infrared analyses of cuts from the effluent of the silica gel column revealed less than 0.01 vol % α-olefins.

STABILITY OF COMPONENTS IN "ULTRASENE"

On the basis of the stability test, the n-paraffins in "Ultrasene" were stable, whereas the nonlinear fraction, even with the aromatic components removed, was unstable. The "Z" numbers obtained were typically those shown in Figure 3. The difference between the "Z" number for the highly branched and cyclic paraffins and that for the slightly branched paraffins was not considered significant.

Although aromatic compounds degraded to form zirconium ligands, the aromatic components in "Ultrasene" were not the principal precursors to zirconium ligands as shown by the instability of the nonlinear fraction after the aromatic components were removed (Figure 3). Two lots of "Ultrasene" that contained different amounts of aromatics were degraded chemically and radiolytically as 30% TBP solvents and tested by the "Z Test" to determine the effect of the aromatic content on stability. The results in Table V show no effect on the stability of "Ultrasene" for aromatic contents differing by a factor of 6.



* Typical "Z" numbers after radiolytic degradation (10^7 rep) and chemical degradation (7days at 70°C) in 4M HNO_3 – 0.2M HNO_2 as 30% TBP Solvents

A "Z" number of 10 was obtained for degraded TBP n-dodecane (Humphrey–Wilkinson, Inc. olefin–free grade).

Typical "Z" number for undegraded TBP-"Ultrasene" mixture was 3.

FIG. 3 STABILITIES OF FRACTIONS FROM "ULTRASENE"

TABLE V

Stabilities of Two Different Lots of "Ultrasene"

"Ultrasene" Lot #	Aromatics, volume % by FIA[a]	"Z" Number Radiolytically Degraded	"Z" Number Chemically Degraded
1	3	300	1000
2	0.5	300	1100

(a) Fluorescent Indicator Adsorption Method, ASTM D-319-56T

Attempts to improve the stability of "Ultrasene" by removing only the aromatic components also were unsuccessful. The data in Table VI show that neither oleum washing nor silica gel treatment improved the stability of "Ultrasene", although both of these treatments removed all of the aromatic compounds as shown by ultraviolet analyses. Although no significant improvement was made in the stability of "Ultrasene" by the removal of aromatics, it is still recommended that Purex diluents have a very low aromatic content ($\ll$ 0.1 vol %). This recommendation is based on the potential of the aromatic compounds to form zirconium ligands as shown in Figure 3 and as reported previously by Dennis.(10)

TABLE VI

Stability of Treated "Ultrasene"

	"Z" Number Radiolytically Degraded	"Z" Number Chemically Degraded
"Ultrasene"	300	900
Oleum-washed "Ultrasene"	350	1000
Silica-gel-treated "Ultrasene"	200	900
n-Dodecane[a]	250	10

(a) The olefin-free grade n-dodecane (Lot 131A) obtained from Humphrey-Wilkinson, Inc., New Haven, Conn. is the most stable hydrocarbon diluent that was tested, and was used as a reference standard during this work.

The stability of the linear components from "Ultrasene" (Figure 3) indicates that n-paraffins in the C_{11} to C_{15} range make superior Purex diluents. If a kerosene could be economically processed by the urea method to yield n-paraffins, the product should be essentially equivalent in stability to n-dodecane.

The identity of the compound type that is the principal precursor of zirconium ligands was not established. The data indicate that the major precursors are in the combined isoparaffin-cycloparaffin fraction.

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APPENDIX - STABILITY TEST

CRITERION FOR STABILITY

In this report, "stability" means the resistance of the diluent to degradation to form ligands that complex zirconium. The diluents were made up as Purex solvents (30 vol % TBP - 70 vol % diluent), degraded and washed as described later, and the "Z" numbers were determined by the "Z Test".(8) In the "Z Test" the degraded and washed solvents were equilibrated with a solution of zirconium tracer and the concentration of zirconium retained after three scrubs with 3M HNO_3 solution was determined by counting an aliquot of the solvent. The HNO_3 scrubs were designed to remove the bulk of the zirconium complexed by TBP. The "Z" number is the number of moles of zirconium retained per billion liters of solvent. The stability of the diluent is inversely proportional to the "Z" number.

DEGRADATION CONDITIONS

The samples were degraded chemically by contacting approximately 2 ml of each with an equal volume of 4M HNO_3 - 0.1M HNO_2 for 7 days at 70°C. The 4M HNO_3 - 0.1M HNO_2 solution was prepared by the addition of 8M HNO_3 to an equal volume of a 0.2M $NaNO_2$ solution and adjusted if necessary. The NO_2^- concentration was determined by the addition of an excess of standard 0.05N ceric ammonium sulfate to the HNO_3-$NaNO_2$ solution, followed by titration of the excess ceric sulfate with standard 0.1 normal ferrous ammonium sulfate. The test materials were contained in 15-mm-OD "Pyrex" tubes, loosely stoppered with plugs of "Pyrex" or "Teflon".

Radiolytic degradation was accomplished by exposure to the level of 10^7 rep ±10% as measured by ceric sulfate dosimetry in a beta-gamma source from irradiated fuel elements. Approximately 2 ml of the sample was sealed in 15-mm-OD "Pyrex" tubes in contact with an equal volume of 4M HNO_3 - 0.1M HNO_2. The residual volume, approximately 15 cc, contained air. The extent of chemical degradation that occurred during radiolysis was not determined but was low. In a typical irradiation, the samples were irradiated to 2.5×10^6 rep/hr (8.4 watt-hr/l) for 4 hours and reached a maximum temperature of 60 ±2°C.

POSTDEGRADATION WASHES

After degradation the organic phase was given single, successive washes with equal volumes of distilled water, 1M NaOH, distilled water, 1M HNO_3, and then repeated washes with distilled water until the washings were neutral. After the samples were washed the extent of ligand formation in the degraded component was measured by means of the "Z Test".(8)

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