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A STABLE DILUENT FOR PUREX PROCESS EXTRACTANTS

by

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ABSTRACT

The chemical stability and physical properties of n-dodecane make it a superior diluent for extractants such as are used in the Purex process. The chemical stability of commercial n-dodecane can be increased by purification with synthetic zeolites (molecular sieves).

CONTENTS

LIST OF TABLES

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INTRODUCTION

Solvent extraction processes of the Purex type employ solvents that are solutions of tri-n-butyl phosphate (TBP) in hydrocarbon diluents. The purpose of the diluent is to reduce the density and viscosity of the extractant and to improve the separation characteristics of mixtures of the solvent with dilute nitric acid.

Purex solvent degrades when used for long periods of time and forms ligands which complex zirconium.(1) These ligands are not removed by normal washing; upon repeated use of the solvent they can accumulate to a point where their slow release of that part of the zirconium for which they have affinity will limit the purity of the Purex products. The ligand formation is due to degradation of the "purified kerosene" diluent ("Ultrasene") when contacted with dilute nitric-nitrous acid solutions.

The purpose of this study was to find a hydrocarbon diluent that would demonstrate maximum stability in Purex usage. The physical properties of such a diluent should include relatively high flash point, low viscosity, and low density.

SUMMARY

N-dodecane was shown to be the most stable diluent among the group of normal and iso-paraffins that were tested. Its stability was 20 to 30 times greater than that of "Ultrasene" when exposed to 0.1M nitrous acid in 0.9M nitric acid at temperatures between 40 and 70°C. Higher homologs in the n-paraffin series were less stable than n-dodecane; branched paraffins were considerably less stable.

Purification of commercial n-dodecane with molecular sieves yielded a product that demonstrated excellent stability through the temperature range of 40 to 70°C, and was equivalent to the high purity n-dodecane that was used as a standard.

DISCUSSION

SOURCE OF THE ZIRCONIUM LIGANDS

An accelerated test showed that TBP did not contribute directly to the formation of ligands for zirconium and that "Ultrasene" produced much larger quantities of the ligands than pure n-dodecane. Solutions of 0.9M HNO_3 and 0.1M HNO_2 were prepared in each of these solvents: 100% TBP, 30% TBP in "Ultrasene," and 30% TBP in n-dodecane. Samples of "Ultrasene" and n-dodecane were placed in contact with equal volumes of 4.0M HNO_3 containing 0.1M HNO_2. One aliquot of each solution and diluent sample was held at 40°C for 72 hours and another aliquot was held at 70°C for a like period of time. All the test materials were contained in amber, glass-stoppered bottles during degradation. After the exposure was completed, the exposed diluent samples were made up to 30% TBP solutions with unexposed TBP and the exposed TBP was made up to 30% solution with unexposed n-dodecane. All the solutions were then washed with dilute caustic and with water to remove alkali-soluble degradation products such as DBP and MBP. The relative amounts of zirconium ligand formed in each of the tested solvent components and solvents were then measured by the "Z" test.* The results (Table I) show that "Ultrasene" was degraded more than n-dodecane or TBP by exposure to the nitric-nitrous acids and that the effect was increased in a TBP solution, probably because of the solubility of nitric and nitrous acids in the extractant.

TABLE I

Formation of Zirconium Ligands in Solvent Components and Solvents

Solvent	Exposed Components‡	"Z" Number After Exposure at 40°C	70°C
30% TBP-"Ultrasene"	"Ultrasene"	110	225
30% TBP-"Ultrasene"	TBP-"Ultrasene"	820	3750
30% TBP-n-dodecane	TBP	22	53
30% TBP-n-dodecane	n-dodecane	4	21
30% TBP-n-dodecane	TBP-n-dodecane	40	110

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‡Exposed 72 hours at indicated temperature to mixture of nitrous and nitric acids as described in text.

CHEMICAL STABILITY OF AVAILABLE DILUENTS

Seven diluents were compared with "Ultrasene" with respect to chemical stability and physical properties (Table II, Page 6). A sample of C_{12} n-paraffin obtained from the Archer-Daniels-Midland Company was the only commercial diluent that met all the requirements satisfactorily. Branched paraffin hydrocarbons were the least stable of the compounds tested. The instability of the sample of Shell n-C_{12}-C_{14}, purified by the urea-occlusion process, was probably due to the incomplete removal of branched paraffins. "Amsco" 125-82 (oleum-treated naphtha) was chemically stable but had a low flash point; this material is apparently different in constitution from "Ultrasene" and "Soltrol" 170 since treatment of these diluents with oleum did not yield a significant improvement in stability.

Olefin-free n-dodecane obtained from the Humphrey-Wilkinson Company was adopted as a reference diluent. Numerous tests of this material demonstrated that it is very stable.

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*In the "Z" test, the solvent is washed to remove alkali-soluble components such as dibutyl phosphate, then equilibrated with a standard solution of zirconium and scrubbed with nitric acid. The residual zirconium is measured and its concentration expressed as moles per billion liters of the scrubbed solvent.(2)

TABLE II

Chemical Stability and Physical Properties of Commercial Diluents

Diluent	Supplier	Source	"Z" Number After 72-hr Exposure of 30% TBP Solution at*		Flash Point Closed Cup °F	Density D^{25}_{25}	Viscosity V^{25}_{25} Millipoise
			40°C	70°C			
"Ultrasene"	Atlantic Refining Company	Refined kerosene	800	3750	169	0.7787	16.2
"Soltrol" 170	Phillips Petroleum Corp.	Branched paraffin mixture. Petroleum by-product.	780	540	190	0.7672	23.1
"Amsco" 125-82	American Mineral Spirits Company	Oleum-washed naphtha	120	85	126	0.7480	12.7
Atlantic propylene tetramer (hydrogenated)	Atlantic Refining Company	C_{12} branched paraffin from hydrogenated propylene polymer	5500	6300	130	0.7610	8.90
Sun propylene tetramer (hydrogenated)	Sun Oil Company	C_{12} branched paraffin from hydrogenated propylene polymer	180	1420	134	0.7535	11.4
Shell C_{12}-C_{14} n-paraffin	Shell Oil Corp.	n-paraffin mixture from petroleum	300	1360	181	0.7565	17.4
C_{14}-C_{16} n-paraffin	Archer-Daniels-Midland Company	n-paraffin mixture of C_{14} and C_{16}. Derived from vegetable oils.	110	250	245	0.7678	27.9
C_{12} n-paraffin	Archer-Daniels-Midland Company	n-paraffin mixture containing some C_{10} and C_{14}. Derived from vegetable oils.	50	90	180	0.7446	13.7
Olefin-free n-dodecane (standard)	Humphrey-Wilkinson Company	Derived from n-dodecanol	40	110	180	0.7435	13.5

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*The "Z" numbers of unexposed 30% TBP solutions in all diluents were between 10 and 20.

PURIFICATION OF N-PARAFFINS BY TREATMENT WITH MOLECULAR SIEVES

A method was developed for the purification of hydrocarbons which are mainly n-paraffins. The process involved the use of synthetic zeolites which are marketed as molecular sieves. The zeolite used was Molecular Sieve 13X*; it contains pores with diameters of 13 Ångstroms. The pore diameter allows free passage for n-paraffins, all of which have molecular diameters of 5-6 Ångstroms, while restricting the diffusion rate of branched and cyclic paraffins, which have larger molecular diameters. More polar molecules, such as olefins, appear to be held on the zeolite by adsorption.

Two different samples of Archer-Daniels-Midland (A-D-M) C_{12} n-paraffin were treated by passage through beds of Molecular Sieve 13X. The data in Table III show that the improvement in stability depends on the original stability of the diluent. The product in both cases was as stable after treatment as the reference diluent, olefin-free n-dodecane.

TABLE III

Effect of Treatment of Commercial n-Dodecane with Molecular Sieves

		"Z" Number‡	
Diluent	Sample No.	Original	After Treatment
A-D-M C_{12} n-paraffin	1	100	50-60
A-D-M C_{12} n-paraffin	2	60	45-60
Olefin-free n-dodecane (control)		50	-----

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‡Exposed as a 30% TBP solution at 70°C for 72 hours in the presence of 0.9M HNO_3 and 0.1M HNO_2

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*Obtained from Linde Air Products Company

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