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EVALUATION OF COMMERCIAL n-PARAFFIN MIXTURES FOR PUREX DILUENT

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EVALUATION OF COMMERCIAL n-PARAFFIN MIXTURES FOR PUREX DILUENT

by

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ABSTRACT

Commercially available mixtures of n-paraffins produced by molecular sieve processes were shown by detailed analysis of composition to be of the high quality necessary for use as diluent in the Purex process. Analyses for aromatic and branched or cyclic paraffin content correlate with measurements of chemical degradation, and serve as a satisfactory test for evaluation of quality of bulk shipments.

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INTRODUCTION

Of commercially available hydrocarbons, n-paraffin mixtures are least susceptible to formation of fission product complexing agents through chemical and radiolytic degradation in Purex service.[1] In 1961, a n-paraffin mixture, "Adakane"* 12,[2] replaced refined kerosene as diluent in the First Purex Cycle at the Savannah River Plant (SRP) and continues to provide excellent process performance after almost five calendar years of service.[3] The high cost of "Adakane" 12 (about 90¢/lb) motivated a search for sources of cheaper n-paraffin mixtures that could be used as the diluent in other solvent systems and for makeup of normal entrainment losses in the Purex process. Laboratory evaluation of typical commercial samples provided correlations between composition and stability and showed that molecular sieve processes were the most probable future source of cheap but adequately pure n-paraffins.[4]

This report gives compositional data for n-paraffin mixtures purchased from two commercial sources that employ molecular sieve processes and summarizes the criteria used for acceptance of bulk shipments of material for use as a process diluent at the Savannah River Plant.

SUMMARY

Mixtures of n-paraffins from molecular sieve processes are commercially available at a cost less than twice that of refined kerosene. Four purchases of these materials were typically >98% n-paraffin and met other compositional and physical specifications for use as a diluent in the Purex solvent extraction process. Future evaluations and purchases of molecular sieve n-paraffins can be made without a chemical degradation test because of increased confidence in correlations between stability and composition.

* Archer Daniels Midland Company trademark.

DISCUSSION

EVALUATION OF TYPICAL SAMPLES AND PURCHASED MATERIALS

In 1963 there was only one known commercial source of molecular sieve n-paraffins. In 1964, a second company started production of n-paraffins by a molecular sieve process mainly for captive use in detergent manufacturing. Samples of typical production lots from each vendor were evaluated to determine that the material would meet Purex process requirements and to confirm the correlations between stability and composition. Four purchases of n-paraffin diluent from these two sources were made between October 1963 and April 1965. At the time of purchase, preshipment samples were tested to ensure that the material being held for shipment would meet purchase specifications. The results of evaluations and specification analyses are summarized in Table I.

TABLE I

Evaluation Data for n-Paraffin Mixtures

Sample	Specification	Evaluation				Purchase			
Date		5/63	9/63	9/64	11/64	12/63	10/64	3/65	4/65
Vendor		A	A	B	B	A	A	B	B
Physical Properties									
Flash Point, °C	70° min	(a)	(a)	75	74	73	72	72	73
Sp Gr, 25°/25°	0.77 max	(a)	(a)	0.752	0.751	0.749	0.748	0.751	0.752
Viscosity, Cp 25°C	2.0 max	(a)	(a)	1.37	1.52	1.3	1.24	1.45	1.56
Composition									
n-Paraffin, %	98% min	94	98	>98	98	99	98	99	>98
Aromatics, %	0.1% max 1964 0.2% max 1965	3.1	0.1	0.09	0.06	0.02	0.1	0.06	0.07
Iso-Cyclo Paraffin,(b) %	-	3	2	<2	2	1	2	1	<2
Olefin, %	0.1% max	(a)	<0.1	(a)	<0.1	<0.1	<0.1	<0.1	<0.1
Instability Ratio(c)	-	24	2.6	1.5	1.5	1.2	1.4	(a)	(a)

(a) Not determined.
(b) 100% minus n-paraffin % minus aromatic %.
(c) Zirconium retention of chemically degraded sample relative to similarly treated olefin-free n-dodecane.

In the initial evaluation, the n-paraffin product of vendor A contained aromatics at an unacceptably high level, typified by sample of 5/63 in Table I. Additional refining for removal of aromatics gave material of acceptable aromatic content (sample of 9/63) and all materials purchased from vendor A were batch refined to meet SRP specifications. One lot (not shown) was rejected because of high aromatic content.

All of the purchased materials were similar in physical properties and easily met those specifications. Variations in n-paraffin content among the various samples were not considered significant because all samples evaluated by the "use test" exhibited stability equivalent or superior to that predicted. The materials from vendor B had a wider

carbon chain distribution and contained larger amounts of C_{15}-C_{17} n-paraffins than did the product from vendor A. Typical carbon chain distributions are shown in Table II.

TABLE II

Typical Carbon Chain Distribution

Carbon No.	% of n-Paraffin Content Vendor A	Vendor B
C_9	<1	<1
C_{10}	8	9
C_{11}	22	16
C_{12}	25	20
C_{13}	27	20
C_{14}	17	17
C_{15}	<1	12
C_{16}	-	4
C_{17}	-	1

CRITERIA FOR SELECTION OF n-PARAFFIN MIXTURES

The principal criterion for evaluation and selection of improved diluents at SRP has been a "use test"[1,2] based on chemical degradation of simulated Purex solvent and subsequent determination of the zirconium retention of the solvent by Garrett's "Z Test."[5] Similar tests have been used elsewhere.[6,7] However, in evaluating n-paraffin materials from molecular sieve processes, "use test" data correlate well enough with compositional data from spectrophotometric and gas chromatographic methods[4] to permit selection of n-paraffins on the basis of composition.

The correlations between instability ratio* and aromatic content or iso-cyclo paraffin content (hydrocarbons other than aromatics and n-paraffins) previously reported[4] can be reduced to the following linear equations:

$$\text{instability ratio} = 0.9 + (7.6 \times \text{wt \% aromatic})$$

$$\text{instability ratio} = 0.9 + (1.1 \times \text{wt \% iso-cyclo paraffin})$$

* The zirconium retention of a chemically degraded sample relative to similarly treated n-dodecane.

Comparison of the instability ratios shows that of the impurities found in such n-paraffin samples, aromatics are about sevenfold more deleterious than nonaromatic impurities.

The materials purchased from both sources should provide equivalent performance as Purex diluent. Because of growth in production capacity to meet the needs of detergent manufacturing, the price has dropped to about $0.50 per gallon. The n-paraffin content at this price is limited to about 98% minimum. If n-paraffins of higher purity or even a single carbon number should become necessary (which is highly unlikely) custom production or special refining in small lots at increased cost will be necessary.

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