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USE TEST COMPARISON OF TBP DILUENTS

by

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USE TEST COMPARISON OF TBP DILUENTS

I. INTRODUCTION

Laboratory tests have shown that Shell E-2342 (the diluent currently used in Purex Plant solvent) is more subject to chemical and radiolytic degradation than some other products which could be used as diluents for tributyl phosphate. Although the evidence is somewhat circumstantial, it is thought that the degradation products of Shell E2342 adversely affect Purex plant operation and efficiency through reduced decontamination and poor solvent clean-up. A more stable diluent could improve plant operation by improving solvent extraction decontamination, thereby decreasing tailend treatment and recycle requirements. Savings in the solvent washing procedure could also result.

Several possible alternate diluent materials have been tested in the laboratory recently.

II. TESTING PROCEDURE

The basic test applied to the diluents was a nitric-nitrous acid degradation followed by determination of fission product distribution at simulated extraction, scrubbing, and stripping conditions. This procedure has come to be known as the "use test." Similar tests have been used in process chemistry work at Hanford for several years. Details of the procedure are given in the Appendix.

III. "USE TEST" RESULTS

The diluents tested may be divided into four general classes: A) Saturated petroleum fractions; B) aromatics; C) alkylation or polymerization products; and D) straight chain hydrocarbons. Results of "use testing" diluents of each class are shown in Table I. The diluents were tested as received. A correspondence between diluent class and its quality can be seen.

A. Saturated Petroleum Fractions

Degraded saturated petroleum fractions extracted more fission products than any other diluent type. This behavior has been attributed to the naphthenic content, which is as high as 70 per cent in Shell E2342 and Pacific Base Oil C (Standard Oil Company of California) and about 20 per cent in Shell Code 82000 and 16550.

B. Aromatics

The single aromatic diluent tested, Penola 100 (Humble Oil and Refining Company) degraded severely (specific gravity rose from 0.864 to 1.035 during standard nitration). Fission product extraction was somewhat lower than that obtained with high naphthene-content diluents, however. Thus the nitration products of aromatic compounds evidently complex fission products less strongly than the nitration products of naphthenes. Penola 100 is unsatisfactory for Hanford Purex use because of its low flashpoint, 113 F.

C. Alkylation and Polymerization Products

These are mixtures of highly branched aliphatic hydrocarbons. Soltrol 170 (Phillips Petroleum Company) is an alkylation by-product. The Ashland Oil Company samples were described as "hydrogenated propylene tetramers." "Use test" results indicate diluents of this type occupy an intermediate position between petroleum kerosene fractions, which have not been specially purified, and normal hydrocarbons.

D. N-dodecane

At the present time n-dodecane is considered to be the optimum diluent. Adakane 12 (Archer-Daniels-Midland) is made from coconut oil and is at least 95 per cent n-dodecane. The standard n-dodecane used in these tests was Eastman technical grade.

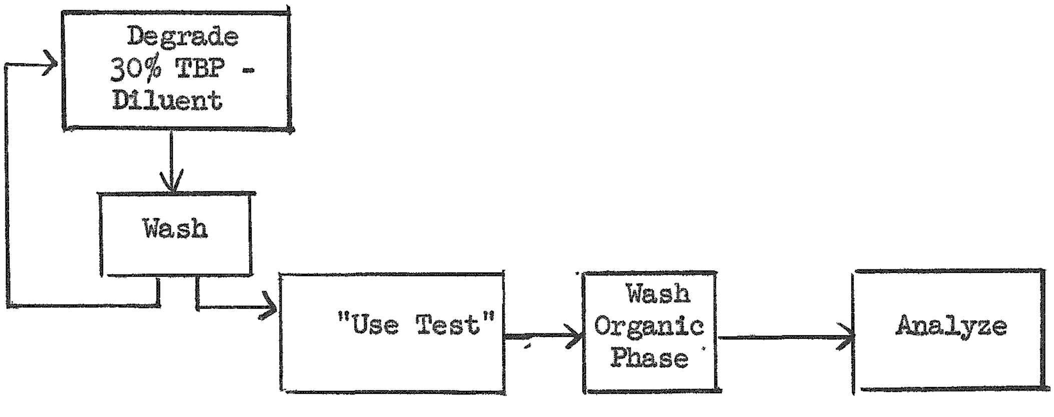
IV. FURTHER TESTING OF PARTICULAR DILUENTS

Two diluents were concentrated upon as candidates for a proposed plant test, Shell Code 85030 (originally designated Code 82000) and Soltrol 170. Code 85030 is a saturated petroleum fraction, similar to E2342 but produced from mid-continent rather than west coast crude. Code 85030 has approximately one-third the naphthene content of E2342. Soltrol 170 is an alkylation product which has been studied extensively at Hanford. A sample of Soltrol recently received from the vendor was used for these tests.

The behavior of the two candidate diluents was compared to that of n-dodecane and E2342 in the laboratory tests.

A. Repetitive Degradations

The principle test of the diluents was a repetitive degradation-wash cycle in which the solvent was "use tested" after each cycle. The basic procedure was as follows:



The solvent degradation portion of the cycle consisted of a 24-hour contact (vigorous agitation) at 60 C with one-half volume 8.0 M HNO_3-0.05 M $NaNO_2$. (Note that the procedure here is somewhat different from that used in the previously described tests. The degradation temperature was lowered to 60C and TBP was added to the diluent prior to degradation.) The wash procedure, used for washing both the degraded solvent and the final organic phase from the "use test", was:

1. 0.025 M $KMnO_4$-2.5% Na_2CO_3 at 50 C.
2. 1.0 M HNO_3
3. 3.0% Na_2CO_3
4. 1.0 M HNO_3

(Equal volume contacts in all cases.)

Four complete cycles were made. The "use test" results and the activity retained in the final washed organic from each cycle are shown in Table II.

In addition to determination of fission product distribution, the following tests were performed on the washed degraded solvent from the fourth cycle.

1. Emulsification Tendency

Disengaging times were determined for simulated first cycle conditions. Results obtained with degraded solvent are compared to those obtained with non-degraded solvent in Table III.

2. Density

Densities of the solvents before and after degradation were measured. These were as follows:

	Initial	After Four Degradation Cycles	Per Cent Increase
E2342 - TBP	0.854	0.904	5.85
N-dodecane-TBP	0.817	0.822	0.61
Soltrol 170-TBP	0.832	0.858	3.12
Code 85030-TBP	0.833	0.855	2.64

3. Sulfuric Acid Treatment

Tributyl phosphate can be separated from diluent by contacting the mixture with concentrated sulfuric acid. This test was performed on the n-dodecane diluted solvent after each cycle to determine if a significant amount of tributyl phosphate was being destroyed during degradation. The volume per cent of tributyl phosphate (plus degradation products reacting with sulfuric acid) remained 30-31 per cent. A much larger quantity of degradation products formed in the other diluents, as indicated by the volume decreases measured upon contacting the fourth cycle solvents with sulfuric acid:

	Per Cent Solvent Volume Decrease
E2342	50.0
N-dodecane	31.0
Soltrol 170	40.0
Code 85030	40.0

B. Radiolysis

A single experiment to compare susceptability to radiolytic damage was made. The diluents were made 30 per cent in tributyl phosphate, carbonate washed, equilibrated with 3.0 M HNO_3-0.01 M $NaNO_2$, and irradiated to a total dosage of 10^8R in a cobalt-60 source. The irradiated solvent was washed and a "use test" performed. The results are shown below:

	Gross Gamma E_a^o			D.F.(1)	
	Extraction	3rd Scrub	2nd Strip	Aqueous	Organic
E2342	0.54	296	318	2400	7.6
Soltrol 170	0.13	47	59	834	14.1
N-dodecane	0.14	1.17	18.7	288	15.4

(1) D.F = gross gamma activity in HAFS/gross gamma activity in final phase

V. DISCUSSION

The apparent order of quality of the four diluents is, from most to least desirable, n-dodecane, Soltrol 170, Shell Code 85030 (82000), and Shell E-2342. These conclusions are based mainly on fission product behavior, considering both distribution ratios and activity retained in solvent after final washing. The magnitude of the differences can be seen in the table below. Here the results given in Table II have been averaged and normalized (dodecane = 1.0).

	Distribution Ratio			Activity in Final Washed Organic
	Extraction	Scrub	Strip	
Dodecane	1.0	1.0	1.0	1.0
Soltrol 170	6.1	3.2	1.6	25.3
Code 85030	15.2	9.7	3.7	319
Shell E2342	31.9	63.1	17.9	2330

In all instances fission product behavior in Soltrol 170 is either approximately midway between the behavior in Shell E2342 and dodecane, or actually nearer that of dodecane. The differences are greatest when the activities of the final washed organic phases are compared. (It should be noted that the final activity of the E2342 washed organic phase averaged 7.7×10^5 uc/gal, after correcting for dilution. In the Purex plant 10^4 uc/gal in washed solvent is considered excessive. Thus, the degradation in the laboratory tests was much greater than the degradation of the bulk solvent in the Purex plant.)

The magnitude of chemical attack upon Soltrol 170 was about the same as the attack on Shell Code 85030, using as criteria, density change and reaction with sulfuric acid. However, the degradation products formed in Soltrol extracted less fission product activity, bearing out the general observation that non-naphthenic diluents are more desirable.

The same order among the four diluents can be seen in the results of the disengaging time tests shown in Table III. Prior to degradation, the disengaging time was independent of the type of diluent used. After degradation the disengaging times of solvents containing E2342, Code 85030, and Soltrol 170, were all higher, in descending order, than dodecane solvent. The increases in disengaging time observed probably do not represent a significant tendency toward emulsification.

APPENDIX

The standard procedure was as follows:

A. Degradation

Equal volumes of diluent and 8.0 M nitric acid-0.05 M sodium nitrite were contacted for 24 hours at 80 C. The solution was stirred vigorously so that at least 50 per cent of each phase was in continuous emulsion.

B. "Use Test"

The nitrated diluent from the degradation step was made 30 per cent by volume in carbonate-washed tributyl phosphate and contacted as follows:

1. One extraction contact, 2.5 ml HAFS plus 1.0 ml 3WB vs 12.5 ml solvent.
2. Three scrub contacts, 2.0 ml HSR vs solvent from extraction.
3. Two strips, 5.0 ml HCX vs solvent from scrubbing.

Composition of simulated Purex streams:

HAFS	1.8 M UNH - 0.66 M HNO_3 (spiked to approximately 0.1 per cent full level dissolver solution).
3WB	0.456 M UNH - 0.06 M $Fe(NO_3)_3$ - 0.12 M H_2SO_4 - 7.19 M HNO_3 - 0.06 M $NaNO_3$.
HSR	0.073 M UNH - 2.33 M HNO_3
HCX	0.01 M HNO_3

Gross gamma (0.45 mev cutoff) distribution ratios were determined for extraction, final scrub, and strip contacts. The gross gamma distribution ratios were roughly equivalent to zirconium-niobium distribution ratios (as obtained by 256 channel gamma ray spectrometer). A comparison may be made in Table I.

TABLE I

"USE TEST" COMPARISON OF TRIBUTYL PHOSPHATE DILUENTS

Diluent	Type	Extraction E_a^o	Scrub E_a^o	Final Strip Contact E_a^o	Final Strip Contact Aqueous D.F.(1)	Final Strip Contact Organic D.F.(1)
Shell E2342	Saturated petroleum fraction	0.307 (0.373)(2)	12.1 (15.1)	38.4 (42.8)	402 (384)	10.3 (9.0)
Shell Code 32000	" " "	0.125 (0.154)	2.80 (3.50)	14.4 (24.4)	543 (925)	45.0 (37.9)
Shell Code 16550	" " "	0.077 (0.080)	2.33 (4.13)	13.7 (18.4)	474 (465)	33.5 (25.4)
Pacific Base Oil C	" " "	0.201	6.39	31.1	413	13.3
Penola-100	Aromatic	0.078	0.608	2.60	205	78.8
Ashland 1 through 16	Branched paraffin	0.049- 0.099	0.88- 2.78	2.80- 8.33	128- 392	24.7- 82.0
Soltrol 170	" "	0.067 (0.033)	1.95 (0.93)	14.2 (15.2)	1090 (1570)	77.0 (75.3)
Adakane 12	Normal paraffin	0.0056	0.140	0.57	4900	8600
N-dodecane	" "	0.0037 (0.0042)	0.135 (0.54)	0.77 (1.08)	38300 (20500)	82600 (18500)

(1) D.F. = activity in HAFS/activity in aqueous or organic phase of final strip contact.

(2) Values in parenthesis are for Zr-Nb, others are gross gamma.

TABLE II

REPETITIVE DEGRADATION - "USE TESTING" OF SOLVENTS

		Non-degraded	First Cycle	Second Cycle	Third Cycle	Fourth Cycle
Shell E2342	Extraction E_a^o	0.001	0.057	0.095	0.088	0.104
	3rd Scrub "	0.10	8.53	27.2	13.8	33.4
	2nd Strip "	∞	13.5	21.6	43.6	45.0
	Washed Org. uc/gal	0.40	420	1110	799	747
N-dodecane	Extraction E_a^o	0.002	0.0028	0.0034	0.0030	0.0017
	3rd Scrub "	0.12	0.237	0.372	0.045(?)	0.375
	2nd Strip "	13.8	1.0	2.70	1.77	1.45
	Washed Org, uc/gal	0	0.22	1.0	0.1	0
Soltrol 170	Extraction E_a^o	0.001	0.016	0.018	0.013	0.019
	3rd Scrub "	0.25	1.14	1.33	0.75	1.04
	2nd Strip "	∞	4.65	3.06	1.73	1.87
	Washed Org. uc/gal	0	1.56	22.9	0.30	8.7
Code 85030	Extraction E_a^o	0.002	0.039	0.049	0.046	0.032
	3rd Scrub "	0.27	1.57	3.24	3.46	4.40
	2nd Strip "	2.3	3.25	4.42	11.0	6.84
	Washed Org. uc/gal	0.22	6.47	96.5	252	66.2

TABLE III

DILUENT EVALUATION: DISENGAGING TIME COMPARISON

Method: Disengaging times were measured after dispersion by 100 strokes, in one minute, of the reciprocating disengaging time apparatus. Equal volumes (12.5 ml) of each phase were used for all contacts.

Contact	Disengaging Time, Seconds(1)			
	E-2342	N-dodecane	Soltrol 170	Code 85030
Solvent vs. syn. HAFS	82 (61)	48 (65)	62 (69)	94 (72)
Same solvent vs. new HAFS	99 (81)	60 (78)	76 (89)	101 (90)
" " vs. syn HSR	80 (59)	46 (70)	60 (65)	70 (69)
" " vs. new HSR	79 (66)	47 (69)	63 (60)	72 (67)
" " " " "	79 (68)	47 (71)	63 (71)	79 (61)
" " vs. HCX	63 (39)	22 (30)	31 (32)	34 (35)
" " " new HCX	47 (24)	15 (17)	27 (23)	29 (23)
" " " " "	47 (20)	14 (15)	26 (20)	26 (18)
" " " " "	60 (21)	12 (17)	32 (21)	32 (19)
" " " " "	115 (24)	17 (18)	31 (25)	58 (24)
" " " " "	120 (29)	18 (19)	31 (26)	105 (27)

(1) Values without parentheses were obtained using solvent degraded by four nitration - wash cycles. Values within parentheses are for corresponding solvents prior to any degradation.