AFRPL-TR-76-23

2

B S.

PREPARATION OF PCDE

FINAL REPORT FOR PERIOD
18 DECEMBER 1974 THROUGH 31 JANUARY 1976

Rocketdyne Division
Rockwell International
6633 Canoga Avenue
Canoga Park, California 91304

Authors: F. C. Gunderloy
B. L. Tuffly
W. W. Thompson
C. L. West
M. D. Robertson

APRIL 1976

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

AIR FORCE ROCKET PROPULSION LABORATORY
DIRECTOR OF SCIENCE AND TECHNOLOGY
AIR FORCE SYSTEMS COMMAND
EDWARDS AFB, CALIFORNIA 93523

NOTICES

FOREWORD

This report was submitted by Rocketdyne Division of Rockwell International, 6633 Canoga Avenue, Canoga Park, CA 91304, under Contract F04611-75-C-0012, Job Order No. 305908K with the Air Force Rocket Propulsion Laboratory, Edwards AFB, California 93523.

This report has been reviewed by the Information Office/DOZ and is releaseable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations. This report is unclassified and suitable for general public release.

NORMAN J. VANDERHYDE, GS-14
Project Engineer

ROBERT L. GEISLER, GS-14, Chief
Propellant Development Branch

FOR THE COMMANDER

CHARLES R. COOKE, Chief
Solid Rocket Division

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(19) REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER (18) AFRPL TR-76-23
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
(6) PREPARATION OF PCDE

5. TYPE OF REPORT & PERIOD COVERED
Final rept
12-18-74-1-31-76

6. PERFORMING ORG. REPORT NUMBER
(14) R-9911

7. AUTHOR(s)
(10) F. C. Gunderloy, B. L. Tuffly, W. W. Thompson, C. L. West, M. D. Robertson

8. CONTRACT OR GRANT NUMBER(s)
(15) F04611-75-C-0012

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Rocketdyne ~~Division~~
Rockwell International
6633 Canoga Ave., Canoga Park, CA 91304

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
JDN 305908 FK

11. CONTROLLING OFFICE NAME AND ADDRESS
Air Force Rocket Propulsion Laboratory
Edwards Air Force Base
Edwards, CA 93523
(12) 49p.

12. REPORT DATE
(11) Apr[redacted]76

13. NUMBER OF PAGES
50

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
(9) Final rept.
18 Dec 74-31 Jan 76

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
difluoramino compounds, poly ethylene oxide; PCDE; PBEP; DEPECH; tetrafluorohydrazine; thermal stability; infrared spectroscopy; gas-liquid chromatography; heterogeneous reaction; solvents: acetonitrile, nitromethane, chlorobenzene, nitrobenzene, N-methyl-2-pyrolidone, acetone, Freon 112, Freon 113, methyl ethyl ketone, methylene chloride; solubilities: tetrafluorohydrazine, DEPECH

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Alternate processes for preparing PCDE, poly 1-cyano, 1-difluoramino ethylene oxide, have been explored. Difluoramination of DEPECH, poly-2,3 epoxy propane, in heterogeneous gas-liquid reactions near atmospheric pressure have been studied as possible alternatives to the homogeneous high-pressure (400 psig) reaction in acetone solvent currently used for the manufacture of PBEP (the PCDE precursor). Other solvents and mixed solvents have been tested as reaction media. Difluoramine generation by hydrolysis of difluorosulfamic acid

20. Abstract (Concluded)

was studied. Difluoramination does occur using the alternative processes, but addition of the NF_2 is less than half the theoretical amount. No solvent reaction media was found that could dissolve both DEPECH and tetrafluorohydrazine in sufficient concentrations to drive the reaction to completion at near atmospheric pressures. Reactions have been conducted in vented continuous flow apparatus as well as in a closed reaction vessel, and have been followed using infrared spectroscopy, gas-liquid chromatography and elemental analyses.

SUMMARY

Alternate reaction processes for preparation of PCDE were investigated. Because none of the alternatives studied yielded products that were completely difluoraminated, none were suitable for an integrated PCDE process and no scaleup studies were undertaken.

Difluoramination of DEPECH, to form PBEP, has been studied as a heterogeneous gas-liquid reaction at pressures near ambient (13.8 to 24 psia). Several solvents and mixed solvents have been tested as reaction media. The reactions have been followed by means of gas-liquid chromatography (GLC) and infrared spectroscopy of the gas phases, and by infrared spectroscopy and elemental analysis of the reaction products. Reactions have been conducted in both closed vessel and vented continuous-flow apparatus. Solubilities of DEPECH and tetrafluorohydrazine (N_2F_4) have been measured in selected solvents. Preliminary work included limited studies of HNF_2 generation by hydrolysis of difluorosulfamic acid (DFSA, F_2NSO_3H), with direct conversion of HNF_2 to N_2F_4 and reaction with DEPECH. Use of AIBN (α,α'azo-diisobutyronitrile) has been investigated as a free radical catalyst to accelerate the difluoramination process using N_2F_4. Two batches of crude PBEP were converted to PCDE and the crude PCDE tested for thermal stability and $-NF_2$ content. Test apparatus and techniques were revised frequently as new needs and problems arose.

CONTENTS

ILLUSTRATIONS

TABLES

INTRODUCTION

This technical report summarizes the work accomplished under Air Force Contract F04611-75-C-0012. The work conducted in the period 18 December 1974 through 31 January 1976 was sponsored by the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base. Mr. N. J. Vanderhyde (MKPA) was the contract monitor. Contributors to this program included: Dr. F. C. Gunderloy, Manager, Process Engineering; Dr. B. L. Tuffly, Program Manager; Dr. W. W. Thompson, Responsible Engineer; Messrs. C. L. West and M. D. Robertson.

The overall objective of this program was the investigation of alternative processes for preparation of PCDE, poly 1-cyano, 1-difluoramino ethylene oxide and evaluation of the best for applicability and suitability to an integrated PCDE process in available Rocketdyne facilities. The alternate processes refer to modifications of the difluoramination step in the manufacturing process described by Shell (Ref. 1) where DEPECH, poly-2-3, epoxy propane is reacted with tetrafluorohydrazine (N_2F_4) to form PBEP (poly 1,2-bis(difluoramino)-2, 3-epoxy propane). Primary emphasis was placed on the formation of PBEP by means other than the homogeneous high-pressure (400 psig) reaction using acetone solvent now in large-scale production.

CONCLUSIONS

DEPECH is difluoraminated by tetrafluorohydrazine at near atmospheric pressure, but difluoramination is incomplete in all cases investigated. Less than half of the theoretically available unsaturated bonds in the DEPECH react with NF_2 radicals. Infrared spectrographic analyses of the reaction products have shown in several cases nearly complete disappearance of the unsaturated bonds, but other data (total fluorine and nitrogen content, weight gained by the DEPECH in the reaction, and amount of N_2F_4 consumed) show that only partial saturation has occurred. The unsaturated bonds that do not add $-NF_2$ apparently are involved in side reactions to produce carbonyl compounds and/or other unidentified products. However, tests made in the closed reactor suggest that the unsaturated bonds may undergo fewer side reactions in the mixed solvents Freon 112 and acetonitrile.

The strong carbonyl band (5.8 microns) indicative of hydrolytic (acidolysis) fission of the polymer persists throughout the series. This carbonyl band is normally found in the PBEP produced by the high-pressure synthesis. According to E. E. Ryder, Shell Chem Co. (private communication) the absorbance of the -C=O band (5.8 micron) in good PBEP should be one-third or less of the absorbance of the -CH band (3.4 microns). The best ratio achieved in our test series was 0.9 in Run 34. The very low molecular weights found in the PCDE prepared are believed to be due to the low molecular weight of the crude PBEP used, which was attributed to acid cleavage of the vinyl ether linkages in DEPECH during difluoramination.

Although continuous-flow techniques are most readily adaptable to production processes, it was found that the closed reactor was preferable equipment in which to study the difluoramination reactions. Shortcomings of the vented continuous flow equipment include:

1. Direct measure of N_2F_4 consumption is not possible.
2. Solvent losses are unavoidable.

3. Total gases are not monitored.

4. Concentration of N_2F_4 in the reaction solvent is not known.

It has been possible with the closed reactor system to estimate the consumption of N_2F_4 in the solvents, observe the relative reaction rates, and sample the gases under equilibrium conditions.

The completeness of difluoramination is related to the relative concentration of N_2F_4 in respect to the DEPECH. Reducing the concentration of the DEPECH in solvents presaturated with N_2F_4 appeared to give more complete difluoramination as judged by the weight gained during reaction. A solvent system in which both reactants are equally miscible is needed to provide an environment of excess N_2F_4 for the DEPECH. Completeness of difluoramination calculated from the total fluorine and nitrogen analyses is comparable to that calculated from the weight gained during reaction.

TECHNICAL DISCUSSION

SOLVENTS FOR DEPECH

The solubility of DEPECH in various solvents was chosen as the initial study in the investigation of alternate processes for preparing PCDE. It was assumed that the concentration of 5.25 wt % DEPECH in solution, as used by Shell (Ref. 1, page 84) with acetone, would be a safe range for the other solvents to be used in this study. This concentration was used as a goal for solvents investigated. Selection of the solvents to be tested (acetone, acetonitrile, nitromethane, chlorobenzene, and nitrobenzene) was based largely on the published information concerning the relative stability of the solvents in contact with tetrafluorohydrazine. Acetonitrile has been shown by Rocketdyne IR&D work to be a good solvent for DEPECH and Harshaw (Ref. 2, page 2) reports it to be very stable in the presence of N_2F_4 at 60 C after long periods of exposure. Nitromethane was shown to be unreactive with N_2F_4 by Esso (Ref. 3) and Olin Matheson (Ref. 4). Chlorobenzene was used by Rohm and Haas (Ref. 5) and Hercules (Ref. 6) for the reaction of unsaturated compounds with N_2F_4 at 70 C. DEPECH solubilities were determined at ambient and elevated temperatures in anticipation of future experiments where DEPECH would be reacted with both thermally and chemically generated NF_2 radicals.

Table 1 shows that none of these solvents would give a 5 wt % solution of the polymer at ambient temperature. In an attempt to dissolve all of the DEPECH, the amount of solvent was increased, however, in no case was 100% solubility achieved. Molecular weight fractionation by partial solution was shown to have occurred in the case of acetone by determining the solubility of the insoluble fraction from a previous experiment. While about 40% of the DEPECH was originally soluble, subsequent treatment of the insoluble material only dissolved about 14%. Thus, it would be necessary to effect complete solution to ensure proper molecular weight distribution of the PBEP product. At ambient temperature, the best solvents were chloro- and nitrobenzene but still more than 40% of the DEPECH remained undissolved and the solution concentration was down to about 3 wt % (Table 1).

TABLE 1. DEPECH SOLUBILITY

(Ambient Temperature)

	DEPECH			
Solvent[1]	wt % Charged	% Soluble	wt % in Solution	wt/Unit Vol. Solvent[2]
A	11.3	36	5.3	4.5
A	11.3	37	5.6	4.7
A	11.3	39	5.7	4.8
A	4.9	48	2.6	2.1
A	11.3[3]	14	2.3	1.9
B	15.5	21	4.0	3.3
B	11.7	41	6.2	5.2
B	11.3	37	5.0	4.1
B	5.2	46	2.4	1.9
C	10.6	24	2.5	2.9
C	8.3	42	4.9	5.8
C	8.2	37	3.6	4.3
C	4.9	47	2.5	2.9
D	9.7	30	3.0	3.4
D	8.3	44	3.7	4.2
D	8.3	44	5.3	6.2
D	6.5	47	3.8	4.4
D	4.9	54	3.0	3.4
E	9.0	25	2.4	2.9
E	8.3	55	5.5	6.9
E	5.0	57	3.2	4.0

[1] A - Acetone, Boiling Point 57C, Density 0.79
B - Acetonitrile, Boiling Point 82C, Density 0.78
C - Nitromethane, Boiling Point 101C, Density 1.13
D - Chlorobenzene, Boiling Point 132C, Density 1.11
E - Nitrobenzene, Boiling Point 211C, Density 1.20

[2] Grams of DEPECH which were dissolved in 100ml solvent.

[3] Insoluble fraction from previous solubility test.

Better results were achieved at 50 C (Table 2) where complete solubility was obtained with chloro- and nitrobenzene. When the temperature was increased to 60 C, acetonitrile and nitromethane also dissolved 100% of the DEPECH to give at least 5 wt % in solution. Therefore, at these temperatures, all the solvents of interest could be used. The more dense solvents provide an added advantage in that more DEPECH per unit volume (last column, Table 2) could be used which would improve the overall efficiency of the process.

DIFLUORAMINE GENERATION

The generation of difluoramine, HNF_2, by hydrolysis of difluorosulfamic acid

$$F_2NSO_3H + H_2O \xrightarrow{H_2SO_4} HNF_2\uparrow + H_2SO_4$$

was studied as a possible intermediate for preparing N_2F_4 or NF_2 radicals with which DEPECH could be difluoraminated. The apparatus was assembled as shown in Fig. 1. The apparatus was designed to serve also for difluoramination of DEPECH, but the reactor was disconnected during the preliminary difluoramine generation studies. The DFSA was hydrolyzed by adding it to water in the generator and the HNF_2 was absorbed in oleum in the primary scrubber to evaluate the generator efficiency. Water was charged to the generator, 30% oleum charged to the primary scrubber feed reservoir, potassium iodide solution charged to the auxiliary scrubber, and a 15 wt % solution of DFSA in oleum was charged to the feed reservoir. Gaseous nitrogen was used as the carrier gas and diluent. The nitrogen gas flow and oleum feed to the primary scrubber were started before the DFSA feed to the generator was started.

Results of the first nine runs are summarized in Table 3. The results show generally poor recovery. The best recovery (75.8%, Run 3) occurred with very low carrier gas flow, but this left a large fraction in the reactor. The most efficient delivery to the oleum scrubber occurred with a carrier gas flow rate of 140 ml/min (Run 5) with the generator temperature near 50 C. Difficulty was encountered in Run 4 with plugging of the fritted glass gas diffuser in the

TABLE 2. DEPECH SOLUBILITY

(50 C)

	DEPECH			
Solvent[1]	wt % Charged	% Soluble	wt % In Solution	wt/Unit Vol. Solvent[2]
A	11.3	69	10.0[3]	8.8
A	11.3	67	12.5[3]	11.3
A	8.8	64	7.3	6.2
A	5.0	76	4.1	3.4
A	4.9	73	4.1	3.3
B	11.4	66	9.3[3]	8.1
B	11.4	67	10.0[3]	8.7
B	6.9	70	5.4	4.5
B	5.0	71	3.9	3.2
B[4]	5.1	100	5.1	4.2
B[4]	6.0	100	6.0	5.1
C	8.8	67	7.4	9.0
C	8.2	80	7.2	8.8
C	5.0	75	4.2	4.9
C[4]	4.9	100	4.9	5.8
C[4]	6.2	100	6.2	7.4
D	8.4	100	8.4	10.1
D	8.3	100	12.2[3]	15.4
D	7.2	100	7.2	8.5
D	5.0	100	5.0	5.8
E	8.2	100	8.6[3]	11.4
E	5.0	100	5.0	6.7

[1] A - Acetone, Boiling Point 57C, Density 0.79
B - Acetonitrile, Boiling Point 82C, Density 0.78
C - Nitromethane, Boiling Point 101C, Density 1.13
D - Chlorobenzene, Boiling Point 132C, Density 1.11
E - Nitrobenzene, Boiling Point 211C, Density 1.20

[2] Grams of DEPECH which were dissolved in 100ml solvent.

[3] Vacuum Filtration - Solution could have supersaturated due to evaporation. All others pressure filtration.

[4] 60C

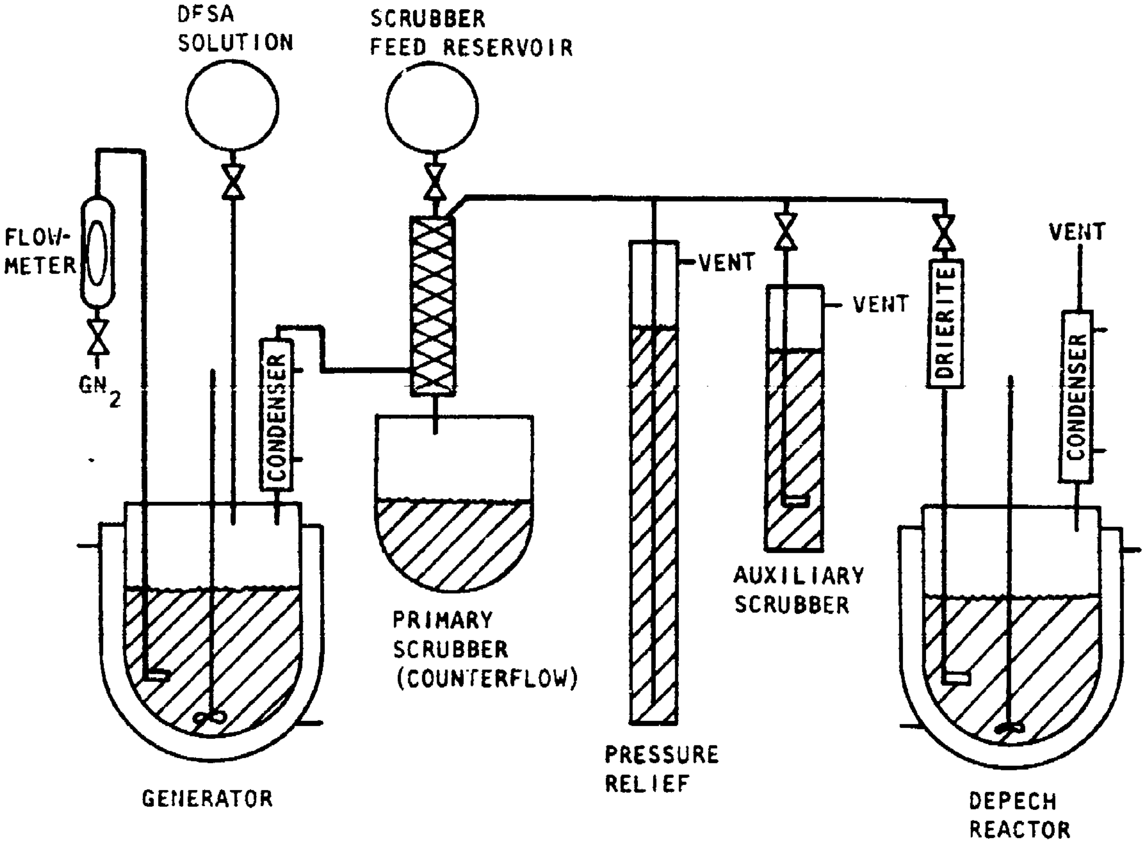


Figure 1. Laboratory Apparatus for N_2F_4 Generation And Reaction

TABLE 3. DIFLUORAMINE GENERATOR SUMMARY

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9
HNF_2 Generator									
DFSA-oleum charge, g	18.7	19.3	19.0	19.5	18.8	20.3	20.4	20.7	20.2
DFSA-oleum feed rate, g/min	1.1	2.1	0.4	0.514	0.457	0.260	0.435	0.390	0.336
Wt.DFSA retained in sol'n, g		0.315	0.78	0.533	0.004	0.03	.076	.081	.453
GN_2 Flow Rate, ml/min	950	470	94	472-94	142	94	94	236	47
Reactor temp., °C	25-50	20	50	50-80	43-53	53-93	50	58	1
HNF_2 Collector (primary scrubber)									
Oleum (30%) feed rate, g/min	3.2	5.1	.01	1.39	1.92	1.51	1.41	1.48	1.72
Oleum Solution final wt, g	90.1	101.3	77.9	156.9	230.8	183.1	149.6	119.8	174.5
% DFSA in oleum	1.7	0.5	1.8	0.34	0.78	0.71	0.54	0.65	0.30
KI-Scrubber (auxiliary scrubber)									
Wt. DFSA absorbed, g		.005[1]	.000	.022	.031	.03	.026	.012	.003
Total F recovered, g							.904	.936	1.135
Percent F recovered							47	47	58
Summary									
DFSA charge, g	2.81	2.89	2.85	2.93	2.81	2.25	1.98	2.19	2.76
DFSA recovery:									
Generator, % of charge		10.9	27.4	0.75	0.15	0.44	3.8	3.7	16.4
Scrubber, % of charge	56.0	16.2[1]	48.4	18.2	63.8	57.7	40.5	35.7	18.8
KI scrubber, % of charge	not used	0.2[1]	0.0	0.75	1.1	1.3	1.3	1.2	0.1
Total, % of charge	56.0	27.3[1]	75.8	19.7	65.0	59.4	45.6	40.6	35.3

---

[1] Diffuser in KI-scrubber plugged, much of gases vented through pressure safety relief.

auxiliary scrubber, which resulted in high pressure (50-inch H_2O) and leakage. Before making Run 5, a perforated glass ball diffuser was substituted for the fritted glass diffuser which reduced the operating pressure to approximately 10 inch H_2O.

Generation of N_2F_4

The possibility of generating N_2F_4 directly during hydrolysis of DFSA was explored, but, before attempting it, a technique for analyzing the gas flow stream by gas chromatography was developed. A gas sample port fitted with a silicone rubber septum was mounted just downstream from the drier and upstream from the reactor in the apparatus shown in Fig. 1. An all-glass 10 cc syringe lubricated with Fluorolube M010 oil was fitted with a valve and a No. 23-gage stainless-steel needle for transport of the gas samples from the test apparatus to the gas chromatograph. The gas chromatograph, F&M Model 700, used a thermal conductivity detector and a 17-foot stainless-steel column 0.131-inch ID packed with 80/100 mesh Poropak-Q. Retention times were measured for a known mixture of gases, which contained N_2, O_2, CO_2, NF_3, N_2F_2, N_2O, CF_4, and NO. The retention times are shown in Table 4.

Generation of N_2F_4 directly by hydrolyzing DFSA in a dilute acidic $Na_2Cr_2O_7$ solution was attempted in Run 10. A 0.5-molar $Na_2Cr_2O_7$ solution was placed in the generator, and the primary scrubber feed was charged with a 0.5-molar $FeCl_3$ solution. Helium was used as the carrier gas in both the reactor and the GLC. No auxiliary scrubber was used. A DEPECH solution (5 wt % in acetonitrile) was placed in the reactor. The system was purged with helium until only trace amounts of air remained as detected by GLC. The gas stream was sampled periodically as the DFSA-oleum was added. Four separate gases were detected. They were identified as N_2, NO, CO_2, and N_2O. The N_2, NO, and CO_2 were generated rapidly with the first addition of DFSA-oleum, and, as the reaction progressed, the concentration of these components diminished while the concentration of N_2O increased. Near the end of the run only N_2O was detected. No N_2F_4 was detected. An IR scan of the DEPECH from the reactor solution showed no $-NF_2$ bands and no detectable change in unsaturation (-C=C-, 6.04 microns).

TABLE 4. GAS RETENTION TIMES IN CHROMATOGRAPH

Column: 17 foot x 0.131 inch ID stainless steel packed with 80/100 mesh Poropak-Q

Column Temperature: 25 C

Carrier Gas: Helium

Detector: Thermal conductivity at 220 C

Gas	Time, seconds
N_2	90
O_2	104
NO	105 to 113
CF_4	166
NF_3	180
CO_2	350 to 380
N_2F_2	380 to 390
N_2O	525 to 570

Four runs (11, 12, 13 and 14) have been made to qualitatively evaluate the gases generated when DFSA-oleum solution was added to water. The first two runs (11 and 12) were conducted in the laboratory glass apparatus (Fig. 1). Water (100 ml) was placed in the HNF_2 generator, 0.5-molar $FeCl_3$ solution was used in the primary scrubber, the auxiliary scrubber was removed, and a 5 wt % DEPECH solution was used in the reactor. A gas sampling port was provided between the Drierite column and the reactor as used for Run 10. Helium was used as the carrier gas in all tests. Gas samples (10 ml) were taken periodically and analyzed in the gas chromatograph. A gas sample for IR spectrographic analysis was taken at the end of Run 12. The gases found in both runs were primarily NO and N_2O with smaller amounts of N_2, NF_3, and N_2F_2. The IR spectra of the DEPECH in the reactor showed no change.

The reaction system was rebuilt as shown in Fig. 2 using a 3-foot helical gas lift contactor for the $FeCl_3$ solution and an 18-inch bubble tower reactor to increase the residence time of the gases in the ferric chloride and DEPECH solutions. A column packed with granular NaF was added to remove any HF generated by the DFSA solution. Runs 13 and 14 were made in the revised apparatus. Both the ferric chloride and DEPECH solutions were sparged with helium gas to remove residual air before each run. Approximately 20 grams of DFSA-oleum solution (~2g. DFSA) was added to 100 ml of H_2O in each run. A solution of DEPECH (125 ml, 5 wt %) in acetonitrile was used in the reactor. Gas samples taken periodically throughout Run 13 analyzed in the gas chromatograph showed that the gases generated included a small amount of N_2F_4 which was masked partially by a baseline shift in the gas chromatogram. A GLC chromatogram from Run 13 is shown in Fig. 3. Appreciable quantities of N_2, NO and N_2F_2 and a small amount of NF_3 were also present. The response of the chromatograph to HNF_2 was unknown, but no unidentified peaks were found that could be associated with HNF_2. "Erratic" performance of the gas chromatograph during Run 14 gave inconclusive data for the gas composition during the run. Further, it was found that the minimum gas sample period (16 to 18 minutes) permitted only one (possibly two) samples to be collected during the N_2F_4 generation period under test conditions. This may also have been a factor in failure to observe N_2F_4 or HNF_2 in earlier runs.

Further study of N_2F_4 generation was set aside since it was apparent that development of a system for continuous generation of N_2F_4 in quantities sufficient to difluoraminate useful amounts of DEPECH would require more time and effort than the study permitted. To expedite study of difluoramination of DEPECH, it was decided to use N_2F_4 available in cylinders at Rocketdyne.

DIFLUORAMINATION OF DEPECH WITH N_2F_4

A series of tests was made based on a heterogeneous (gas-liquid) process using gaseous N_2F_4 and DEPECH dissolved in selected solvents. Use of bottled N_2F_4 permitted continuous runs with a uniform supply of N_2F_4. The first tests (runs 15, 16, 17, and 18) used N_2F_4 diluted with helium, a safety precaution later found to be unnecessary. Acetonitrile was selected as the reaction medium for the initial series of difluoramination tests. The major portion of

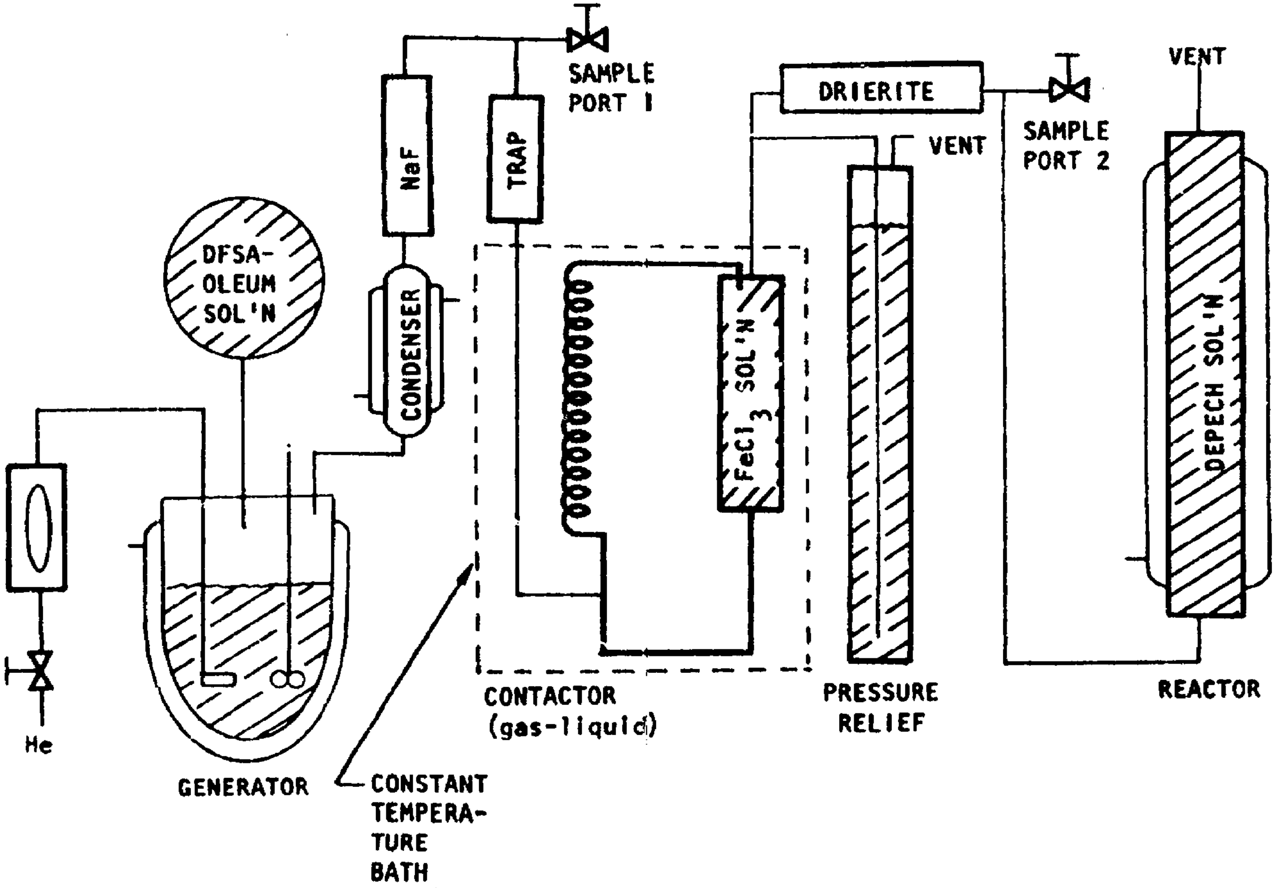
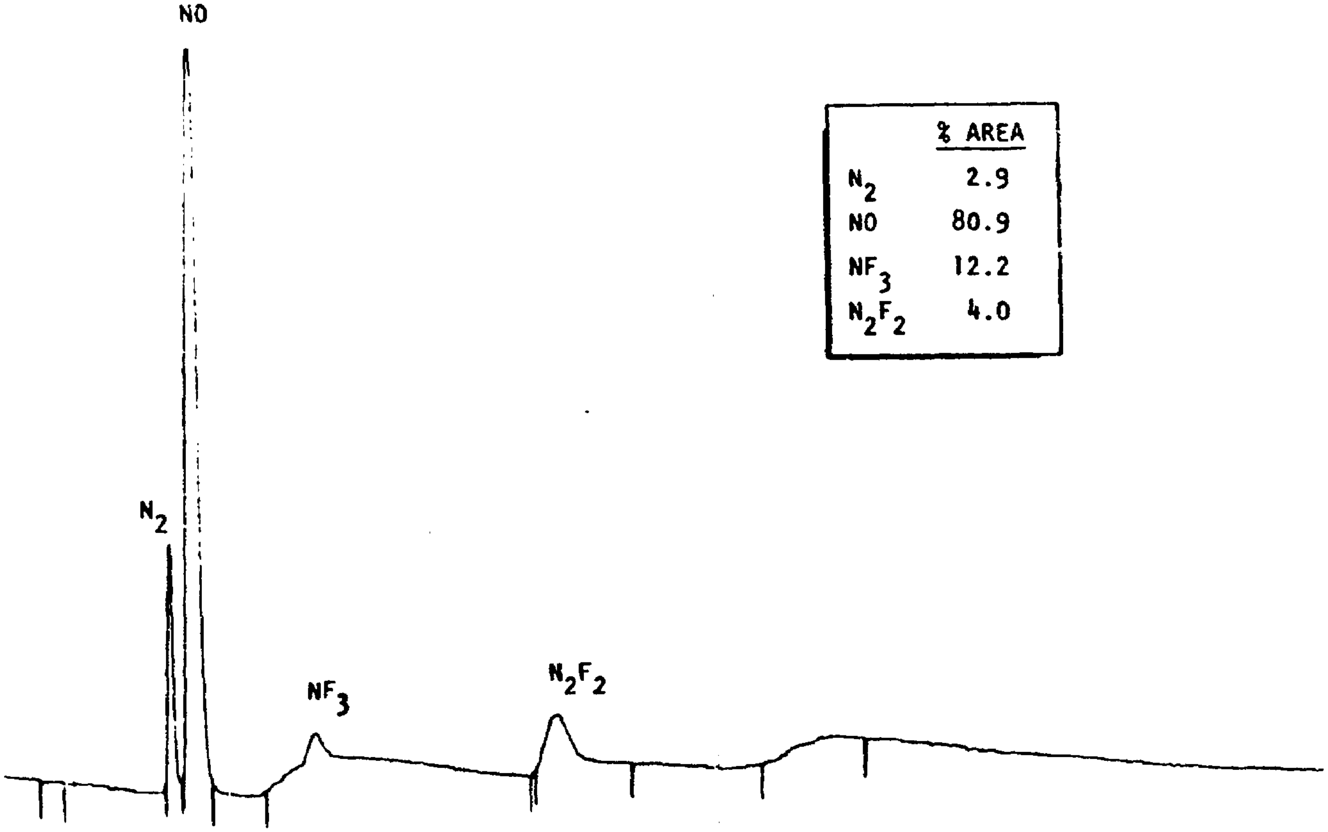


Figure 2. Revised Laboratory Apparatus for N_2F_4 Generation and Reaction



	% AREA
N_2	2.9
NO	80.9
NF_3	12.2
N_2F_2	4.0

Figure 3. Gases From Hydrolysis of DFSA (Run 13)

the series (Runs 16 through 39) was conducted using vented, continuous flow apparatus (Fig. 4 and 5). The final six tests (Runs 40 through 45) were conducted in a closed vessel reactor (Fig. 6) at slightly increased pressure (up to 24 psia). Test conditions and the apparatus type used for each difluoramination test are listed in Table 5.

Run 15 used bottled N_2F_4 in place of the generator with the apparatus shown in Fig. 1. The N_2F_4 bottle was connected just before the NaF column. Ferrous chloride (2-molar) solution was used in the gas-liquid contactor (in place of ferric chloride) to remove NO. Results from this first test showed a decrease in the N_2F_4 concentration and an increase of NO downstream from the $FeCl_2$ contactor. The IR spectrograph (Fig. 7) of the DEPECH reaction product (a dark viscous liquid) showed that reaction did occur. A strong absorption band appeared at 5.8 microns (carbonyl, -C=O) and the band at 6.2 microns (unsaturation, -C=C-) was greatly diminished.

A broad band at 11.3 microns was interpreted as absorption of the $-NF_2$ group. The IR spectrogram (Fig. 8) for DEPECH is shown for comparison. For Run 16 and subsequent tests, the apparatus was modified as shown in Fig. 4. The bubble tower reactor was replaced by the helical gas lift contactor to provide more efficient gas-liquid contact and reduce plugging by DEPECH gel at the gas inlet port of the reactor. The helical gas lift reactor did not completely eliminate plugging, but it could be easily backflushed to remove the gel without terminating the run. The $FeCl_2$ contactor was eliminated. Drierite was used in place of the molecular sieve shown in Fig. 4. The general procedure consisted of charging the DEPECH solution (50 ml of 5 wt % DEPECH) to the reactor, purging the system of air with helium until samples of gas taken from the flow stream at sample port No. 2 showed no air and then flowing excess N_2F_4 through the system under controlled temperature conditions. The gas stream was sampled periodically (approximately 15 minute intervals) throughout the run.

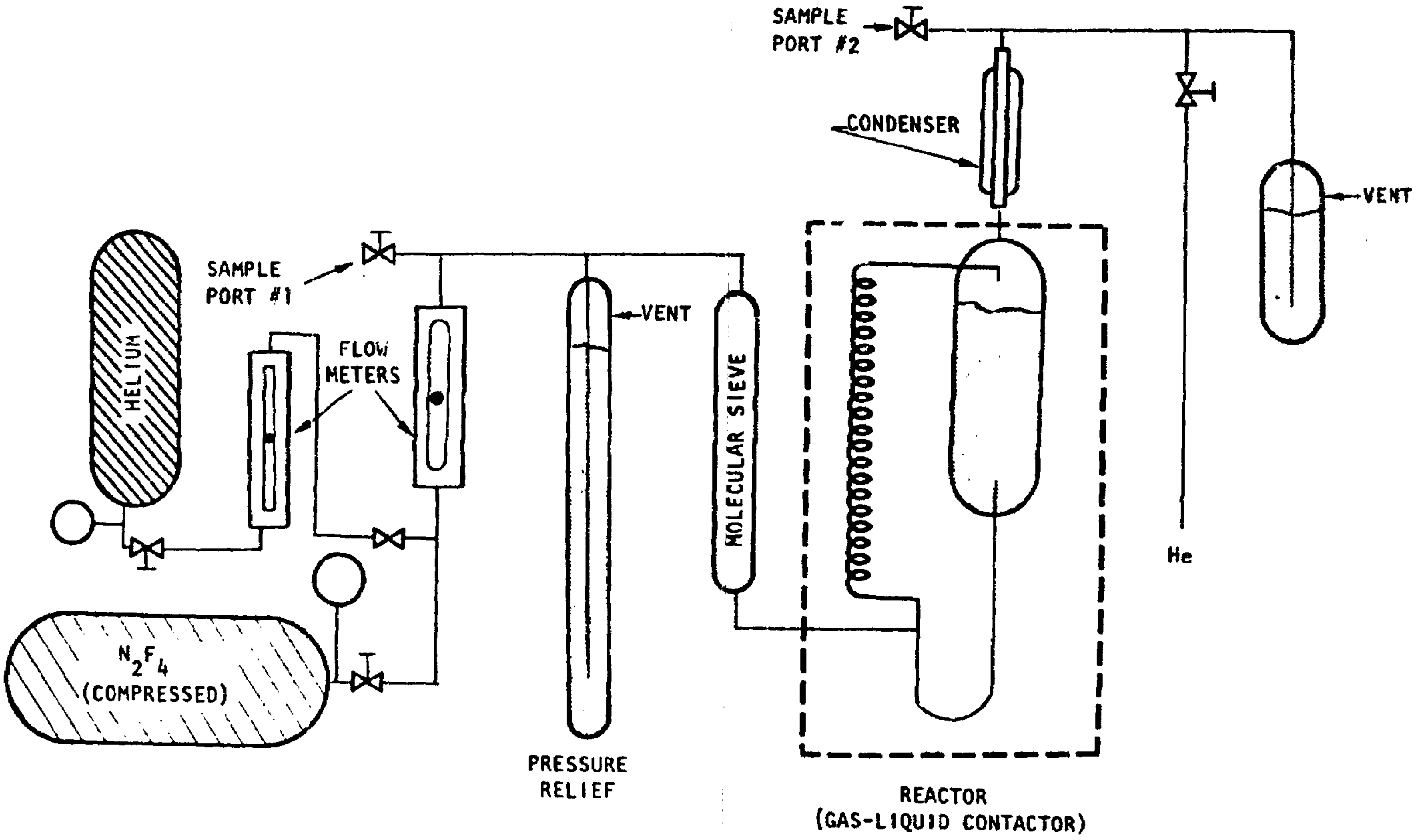


Figure 4. Laboratory Apparatus for Difluoramination of DFPECH

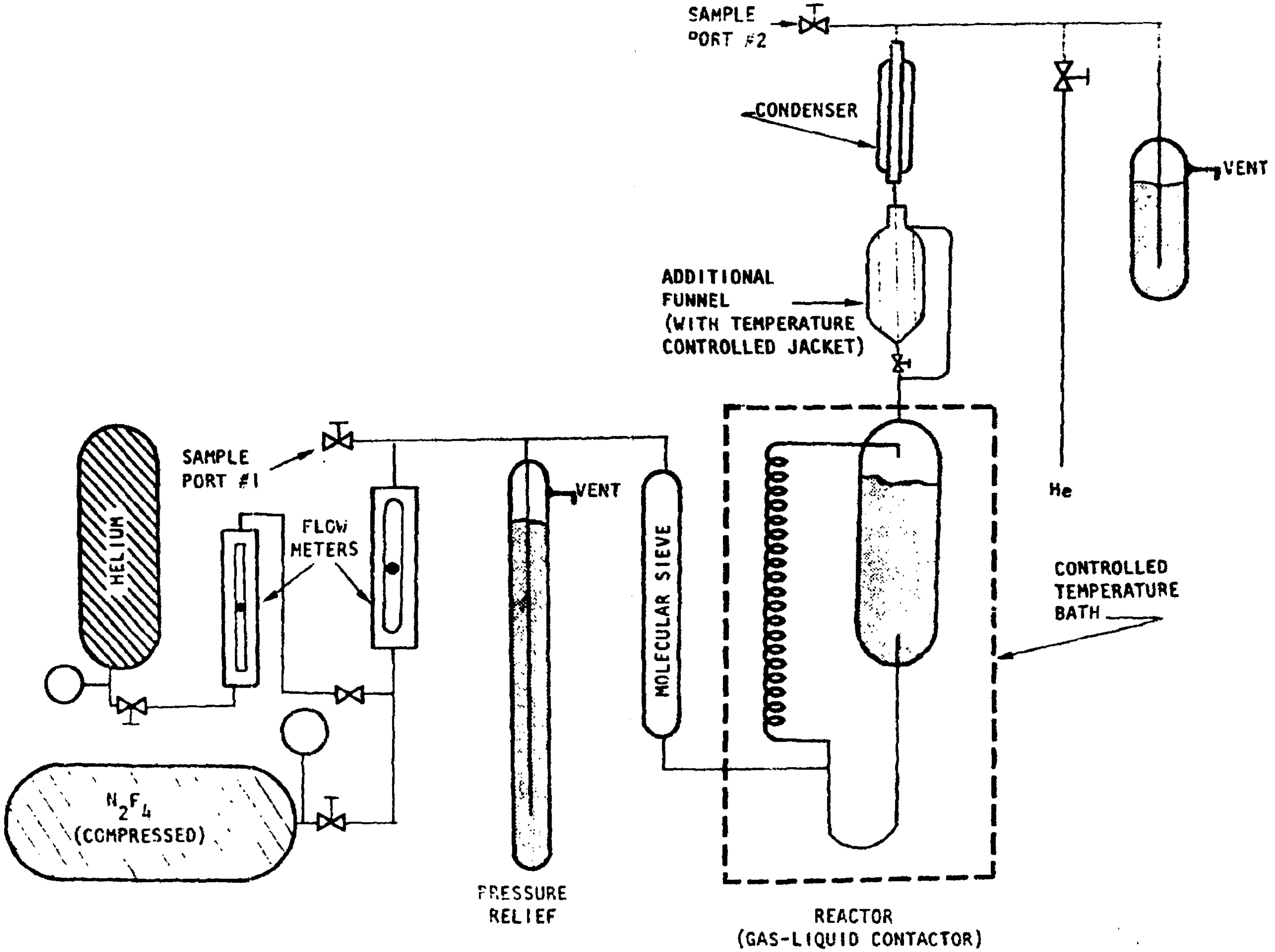


Figure 5. Laboratory Apparatus for Difluoramination of DEPECH

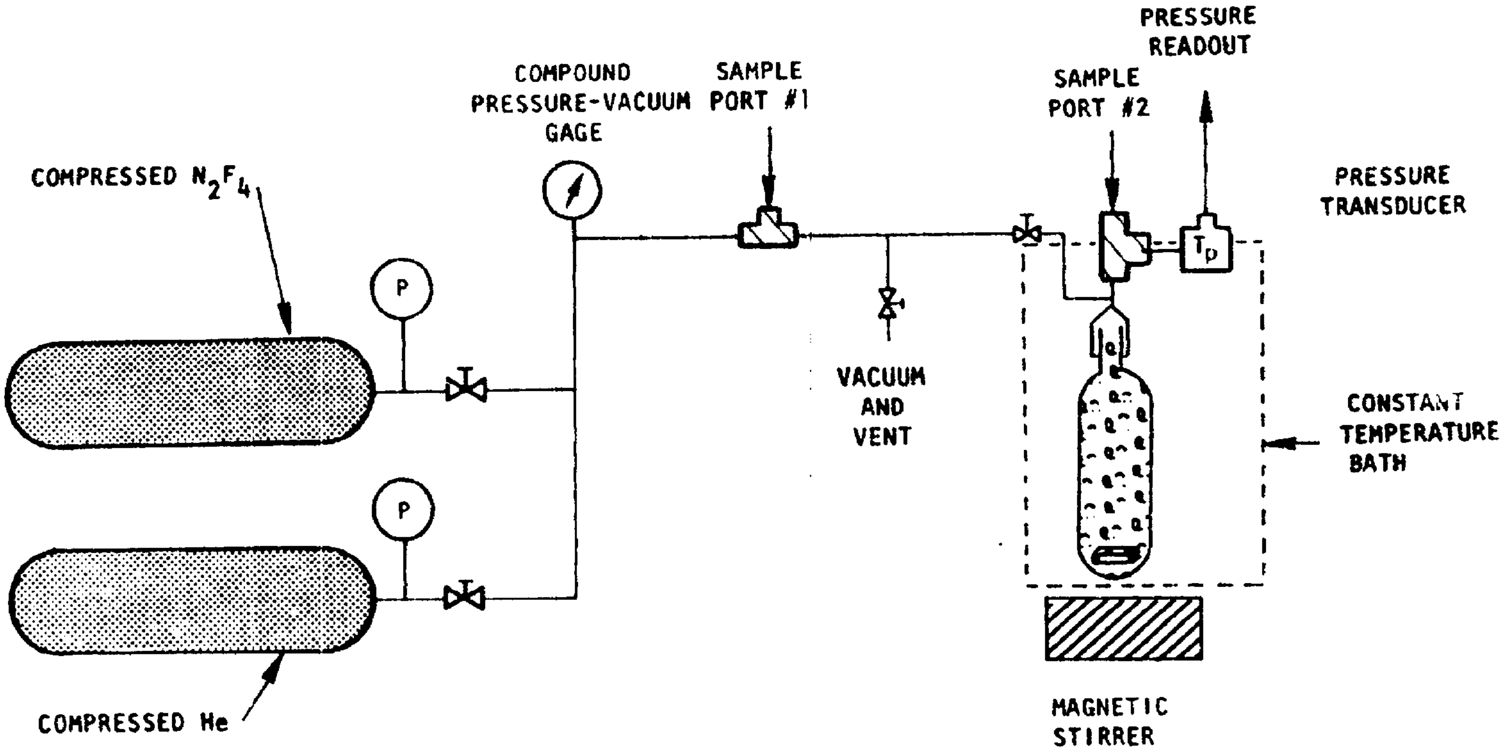


Figure 6. Closed Vessel Reactor Apparatus

TABLE 5. DIFLUORAMINATION TEST CONDITIONS USING N_2F_4

Run	Solvent	Temperature °C	Run Time (hrs)	Equipment	Notes
15	CH_3CN	55	2½	Figure 2	$FeCl_2$ in contactor, N_2F_4 diluted with He.
16	"	53	2	Figure 4	N_2F_4 diluted with He, Drierite instead of mol siev
17	"	60	2	"	" " , no mol. sieve.
18	"	60	-	"	No DEPECH charged, NO not removed by mol.sieve.
19	"	60-70	3	"	50ml 5%w DEPECH in CH_3CN.
20	"	60	2	"	50ml 5%w DEPECH + .05%w AIBN in CH_3CN.
21	"	70	1½	"	50ml 5%w DEPECH in CH_3CN.
22	"	70	2	"	
23	"	80	2	"	" " "
24	"	70	4	"	" " "
25	"	70	6	"	" " "
26	CH_3CN/CH_2Cl_2(9/1)	70	4	"	50ml 3%wDEPECH in CH_3CN/CH_2Cl_2(9/1)
27	CH_3NO_2	70	4	"	50ml 5%w DEPECH in CH_3CN
28	CH_3CN	70	4½	"	50ml 5%w DEPECH in CH_3CN
30	"	80	6	See text	" " "
32	"	60		Fig. 5	Addition funnel for DEPECH sol'n added.
33	Me-pyrrol.[2]	60	2	"	15ml 20%w DEPECH in Me-pyrrol.
34	Me-pyrrol.[2]	60	5	"	15ml 20%wDEPECH + 0.2%wAIBN in Me-pyrrol.
35	Me-pyrrol/ Freon TF[3](1:4)[2]	55	4½	"	15ml 20%DEPECH in Me-pyrrol.
36	Me-pyrrol[2]	80	2½	"	" " "
37	"	70	3	"	15ml 20%wDEPECH + 0.2%wAIBN in Me-pyrrol.
38	Freon 112[4]	70	3½	"	15ml 20%w DEPECH in Me-pyrrol.
39	"	sat'd at 28° raised to 80°	2	"	5ml 20% DEPECH in Me-pyrrol.
40	CH_3CN	70		Fig. 6	N_2F_4 partially lost during addition of DEPECH.
41	CH_3CN	70	3-2/3	"	10ml 5%w DEPECH in CH_3CN
42	"	70	4	"	10ml 5%wDEPECH + .05%w AIBN in CH_3CN
43	Freon 112[4]	70	4-3/4	"	10ml 5%wDEPECH in CH_3CN
44	"	70	4½	"	" " "
45	MEK[5]	70	4½	"	10ml 5%wDEPECH in MEK

---

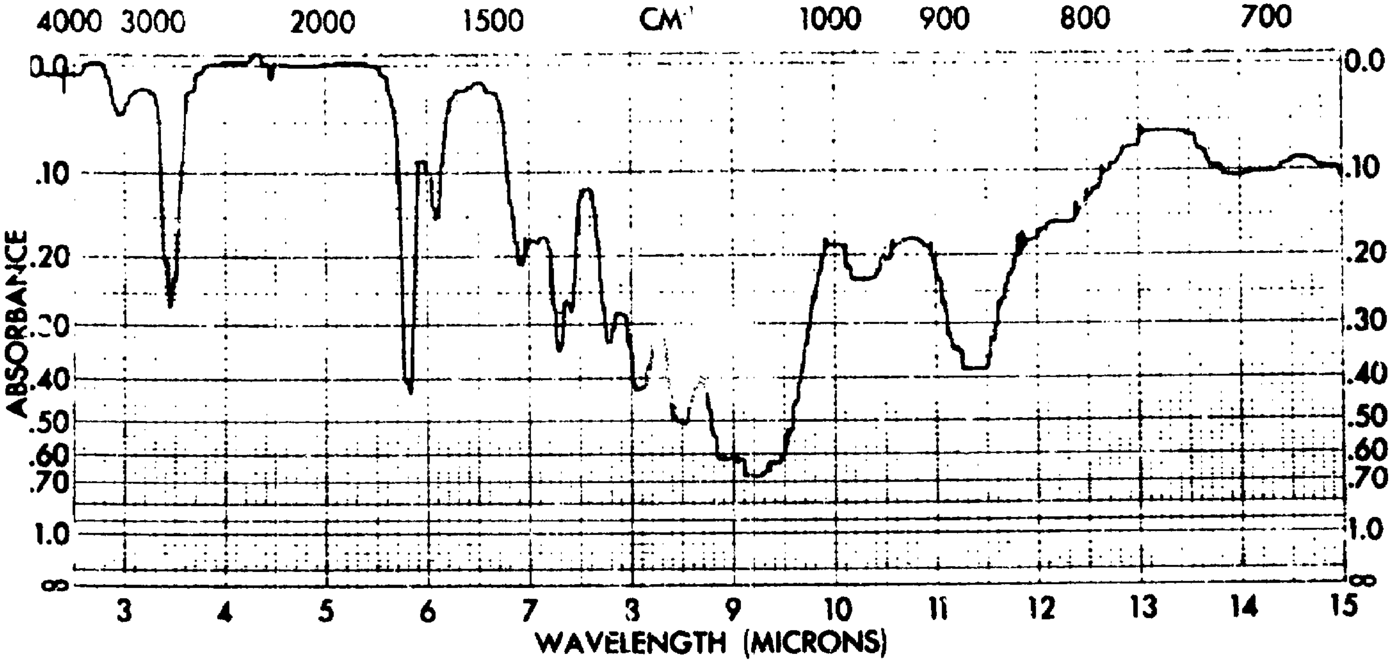
[1] α,α′-azo-di-iso-butyronitrile

[2] N-methyl-2-pyrrolidone

[3] FCl_2CCClF_2

[4] FCl_2CCCl_2F

[5] Methyl ethyl ketone

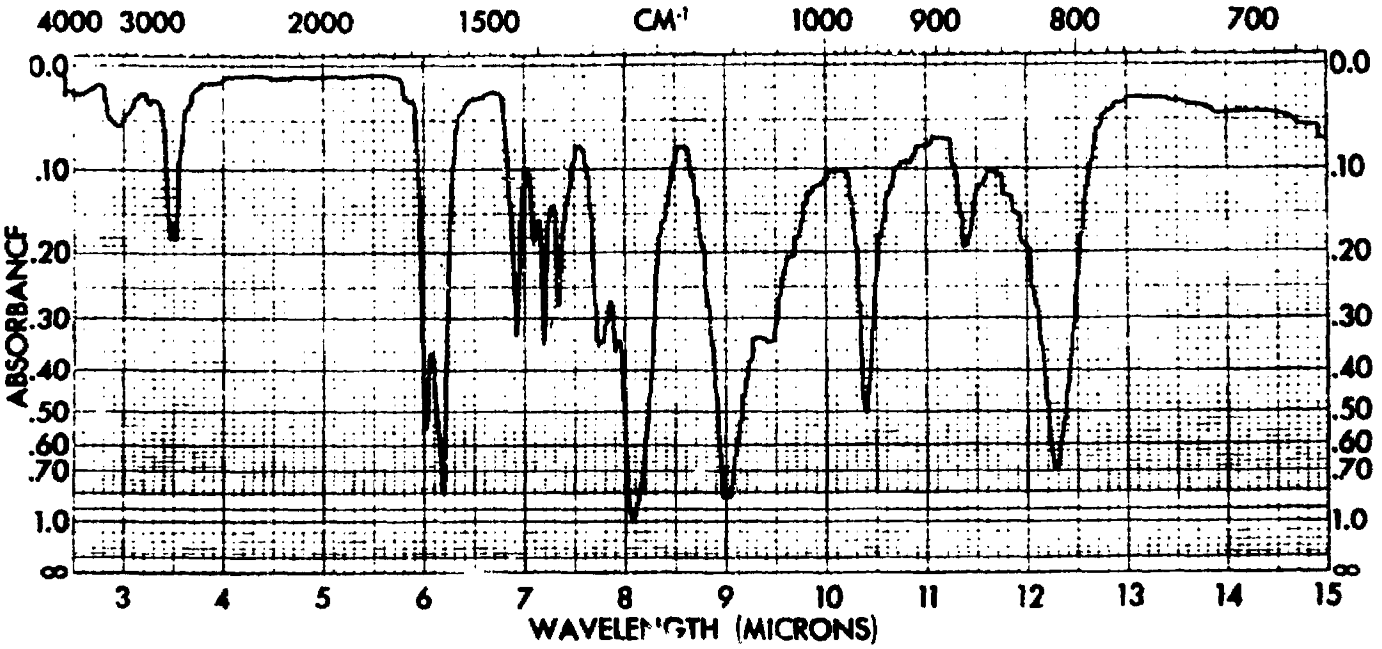


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE REACTION PRODUCT DEPECH WITH N_2F_4 CRUDE RUN 15		1.	FILM ON NaCl WINDOW, MAY HAVE TRACE OF ACETONITRIL
	PURITY UNK	2.	
	PHASE VISCOUS LIQUID	DATE 3 JULY 75	
	THICKNESS UNK	OPERATOR C. L.	

SPECTRUM NO.
SAMPLE

Form 610-C-161 Nov 9-65

Figure 7. IR Spectrograph of DEPECH (Run 15)



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE DEPECH		1.	FILM ON NaCl PLATE FROM CH_3CN SOL'N USED FOR DIFLUORAMINATION OF DEPECH WITH N_2F_4 RUN 17, 14 JULY 75
	PURITY UNK	2.	
	PHASE SOLID	DATE 14 JULY 75	
	THICKNESS UNK	OPERATOR C. L.	

SPECTRUM NO.
SAMPLE

Form 610-C-161 Rev 9-65

Figure 8. IR Spectrogram For DEPECH

The gas-sample handling techniques were revised as a result of gas chromatographic data from Runs 17 and 18. Gas samples taken during Runs 17 and 18 were found to have been contaminated by air during transport of the samples from the reactor to the gas chromatograph. With the improved technique, the analyses of samples of supply N_2F_4 taken at either sample port were identical with the same N_2F_4 fed directly to the gas chromatograph from the supply cylinder.

The N_2F_4 from the supply bottle was reanalyzed and found to be 93.2 area % N_2F_4. 2.1% N_2, 0.3% NO, 3.0% NF_3, and 1.5% N_2F_2. A new cylinder of purer N_2F_4 was procured before Run 18, which analyzed 97.6 area % N_2F_4. 0.4% N_2. 0.4% NO, 1.0% NF_3, 0.1% N_2F_2, and 0.8% N_2O. A typical GLC chromatogram for N_2F_4 is shown in Fig. 9.

No dilution of N_2F_4 was used in Run 19 and all subsequent tests. Runs 19 through 25 were used to explore the effects of increased temperature (up to 80 C) and increased reaction time (up to 6 hours) upon difluoramination of DEPECH in acetonitrile. The catalyst AIBN was used in Run 20 at a concentration of 1% of the DEPECH with little effect, as shown by the IR spectrogram (Fig. 10).

Elemental analyses of the DEPECH reaction products for total fluorine and total nitrogen contents are summarized in Table 6, along with those for an old sample of Shell PBEP (sample 9557-80). The percentage of the unsaturated bonds which have been reacted are compared assuming a theoretical value of 60 wt % NF_2 content for totally difluoraminated PBEP. The fluorine-to-nitrogen mole ratio of the reaction products agree closely with the theoretical ratio of 2.0, and suggests that difluoramination had occurred with no fluorination side reaction. Increased temperature and increased reaction times (Run 25, 6 hours) gave the greatest difluoramination, approximately 46% of theory.

Substitution of methylene chloride for approximately 10% of the acetonitrile solvent (Run 26) gave less satisfactory results. The presence of mixed solvent CH_3CN/CH_2Cl_2 did not dissolve the DEPECH as readily as the acetonitrile alone; therefore, the concentration of the reaction solution was reduced to approximately 5 wt %. A more serious effect of the mixed solvent is reflected in an F/N mole ratio greater than 2.0, which indicates that some fluorination of the DEPECH may have occurred.

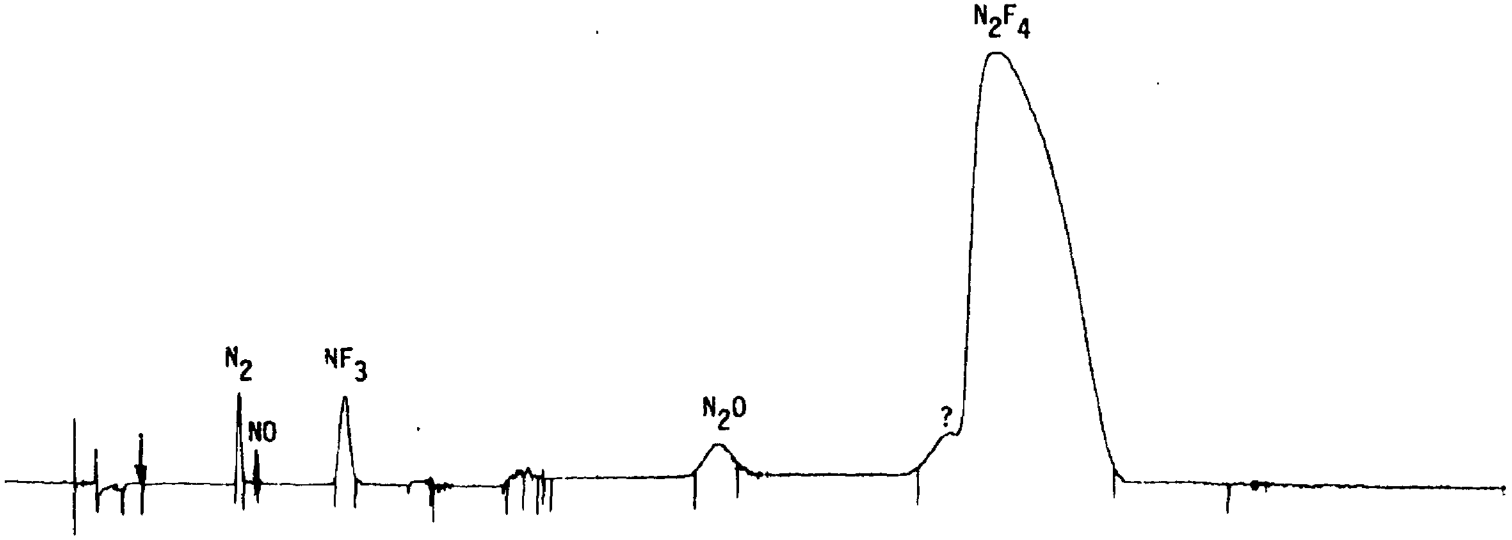
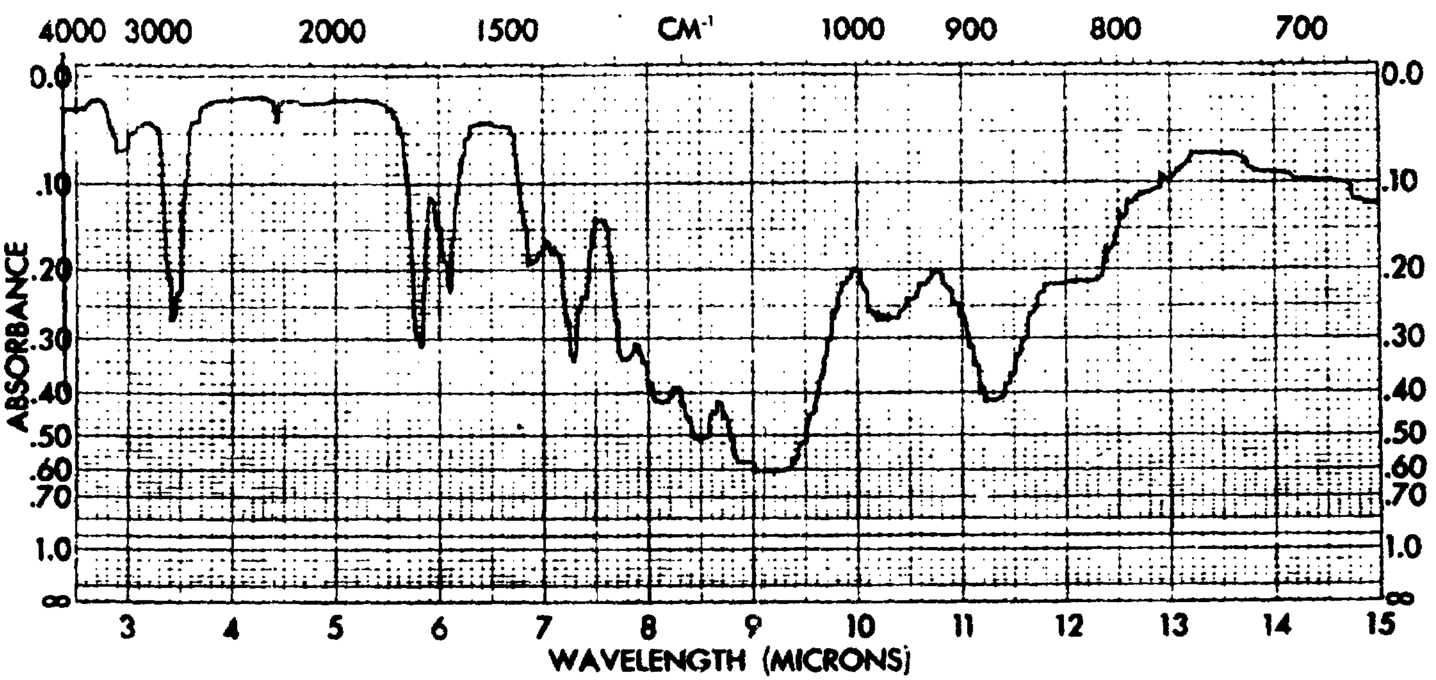


Figure 9. GLC Chromatogram of N_2F_4



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE Reaction product DEPECH + 1% AIBN after reaction with N₂F₄ at ~~80°C. for 2 hrs at~~ atm. press		1.	Film on NaCl plate from CH₃CN sol'n
	PURITY unk	2.	
	PHASE Liquid (viscous)	DATE 29 July 75	
Run 20 scan 3	THICKNESS unk	OPERATOR C LeWest	

SPECTRUM NO.
SAMPLE

Form 610-C-161 Nov 9-65

Figure 10. IR Spectrogram of DEPECH (Run 20)

TABLE 6. ELEMENTAL ANALYSES OF DEPECH REACTION PRODUCTS

Run	Total F % w	Total N % w	F/N Molar Ratio	NF_2 % w	% Saturation
19	15.04	5.59	1.98	20.6	34
20	12.06	4.45	2.00	16.5	28
24	19.15	6.82	2.07	26.0	43
25	20.33	7.22	2.07	27.6	46
26	16.67	5.47	2.25	22.1	37
27	16.75	6.04	2.04	22.8	38
30	17.66	7.27	1.80	24.9	42
36	11.96	8.74	1.01	20.7	35
37	12.77	7.46	1.26	20.2	34
38	16.08	8.54	1.39	24.6	41
PBEP, Shell 9557-80	38.00	15.98	1.75	54.0	90
Theoretical, assuming M.W. ≈3600 for PBEP			2.0	60	100
Specifications for PBEP				>57	

Nitromethane was used as the reaction solvent in place of acetonitrile in Run 27. The amount of difluoramination was slightly less than for comparable conditions using acetonitrile, and the F/N ratio did not indicate any fluorination had occurred. However, the presence of O_2 and relatively larger amounts of N_2O in the vent gases suggested the mixture was less stable than acetonitrile in the presence of N_2F_4.

Analysis by gas chromatography of the vent gases from the reactor taken at sample port No. 2 was followed throughout the runs to evaluate reaction differences. Using periodic samples, it was possible, when acetonitrile was used as the solvent, to observe the appearance of increased amounts of N_2 in the gas stream before any N_2F_4 was detected. The N_2 content reached a maximum shortly after the N_2F_4 was detected and diminished continuously until at the end of the run the vent gases approached the same analysis as the N_2F_4 gas supply sampled at port No. 1 prior to difluoramination. A change in NF_3, a minor component (<1%), followed the increase and decrease of the nitrogen during the run, suggesting that a small amount of N_2F_4 disproportionates according to the equation:

$$3N_2F_4 \rightarrow 4NF_3 + N_2$$

Throughout the run the NO content at port No. 2 remained below that found in the N_2F_4 supply. When the N_2F_4 supply was stopped and the reaction product purged with helium, increased amounts of NO were found even after all N_2F_4 was gone. The source of the NO was not identified, but its delayed removal may have been due to its greater solubility in the reaction mixture. Since O_2 and increased amounts of N_2O were found during Run 27 (CH_3NO_2 used as solvent), a control test was made using nitromethane only with no DEPECH and the same procedures with N_2F_4. Relatively small amounts of N_2, no O_2, and only moderate increases in NO were observed.

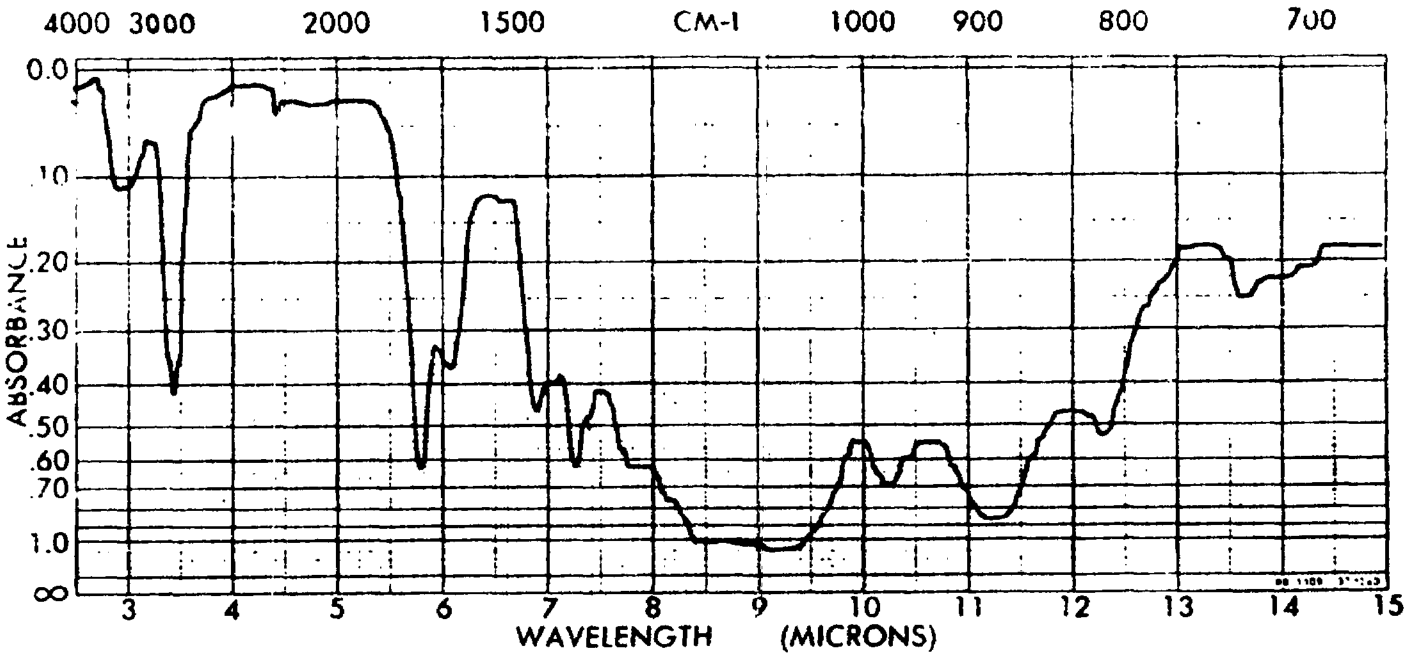
An attempt was made to convert the crude PBEP from two runs (28 and 30) to PCDE (Runs 29 and 31, respectively). The DEPECH reaction products in the actonitrile solvent were dehydrofluorinated using a procedure approximating that described by Shell (Ref. 1, page 181). The reaction solution was purged of N_2F_4 with helium in the reactor, added to 50 ml of CH_2Cl_2, washed with water, and dried by passing the CH_2Cl_2, solution over 4A molecular sieves. The CH_2Cl_2 content of the product solution was adjusted so that the PBEP concentration was approximately 11.2 wt % and added rapidly to an acetone solution of TMA (trimethylamine, 11.2 wt %) containing a 20% excess of TMA. The reaction mixture was stirred for 5 minutes with the temperature controlled between 20 and 22 C. The excess TMA was neutralized with dilute HCl, the CH_2Cl_2 solution washed with water, and dried over 4A molecular sieves.

Thermal stability, elemental analysis and molecular weights of the crude PCDE products were determined:

	Run 29	Run 31
Thermal stability, cc/g/100 hours	Ts_{120}=7000	Ts_{120}=1600
Molecular weight (VPO)	450	500
Total fluorine, wt %	13.66	11.27
Total nitrogen, %	7.42	6.56
F/N molar ratio	1.36	1.26

Both products showed very weak absorbance at 4.45 microns (-C≡N). Their poor thermal stability is characteristic of incomplete dehydrofluorination.

Infrared spectrograms of the products from Runs 28 (Fig. 11) and Run 29 (Fig. 12) show the poor quality. The IR spectrum for good PCDE (Fig. 13) is given for comparison.

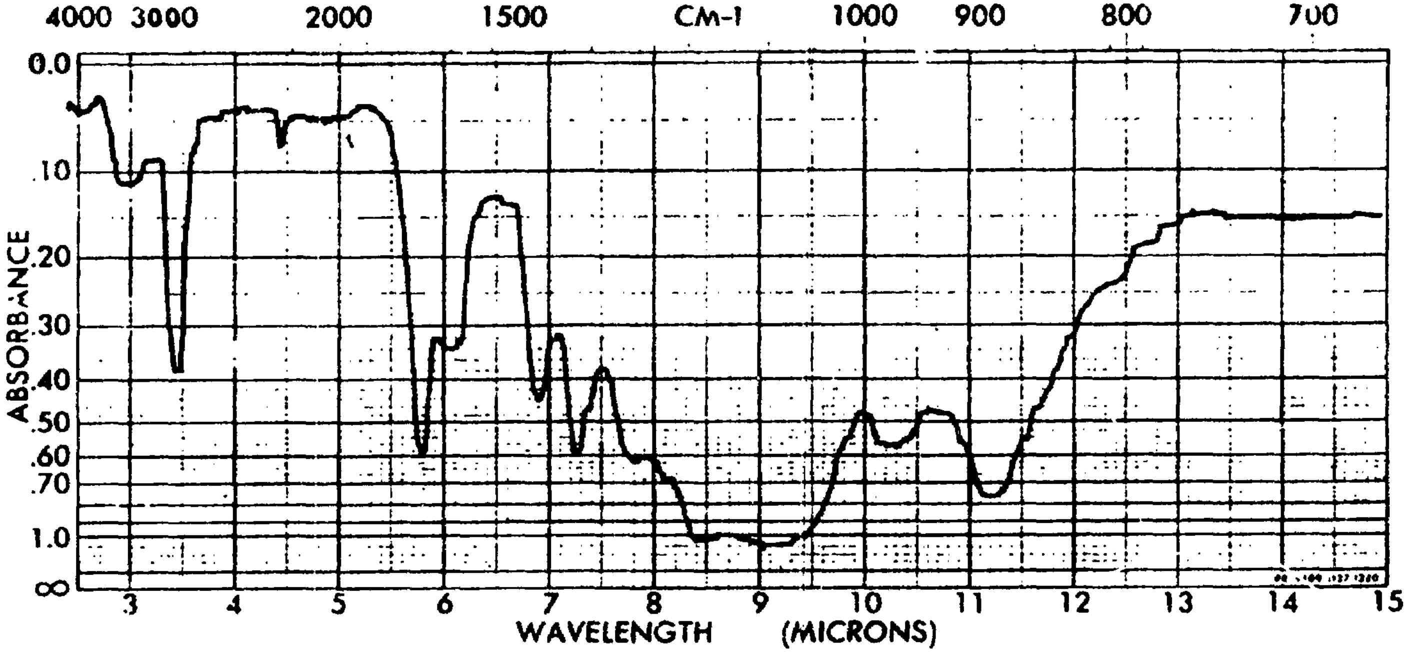


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS FILM ON NaCL PLATE FROM WASHED CH_2Cl_2 SOLN.
SAMPLE REACTION PRODUCT DEPECH WITH N_2F_4 4 HRS AT 70°C TAKEN UP IN CH_2Cl_2 AND WASHED WITH H_2O AT END OF REACTION PERIOD RUN 28		1.	
	PURITY UNK	2.	FAST SCAN RATE
	PHASE LIQUID	DATE 26 AUG 75	
	THICKNESS ~1 MIL	OPERATOR C.	

SPECTRUM NO.
SAMPLE

RECORDING CHARTS

Figure 11. IR Spectrogram (Run 28)

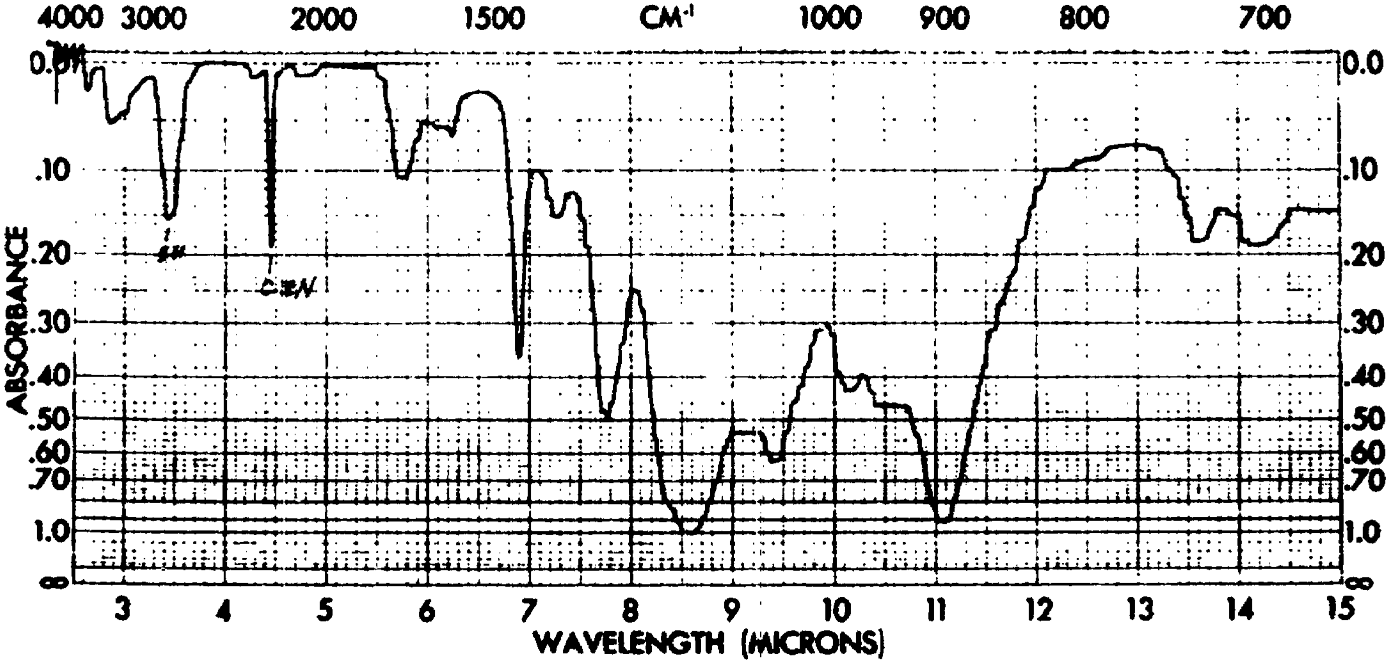


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS Film on NaCl plate
SAMPLE Reaction product PBEP-26 treated with TMA after 76 hrs stripping under GN2		1.	
	PURITY UNK	2.	
	PHASE LIQUID	DATE 2 SEPT. 75	
RUN-29	THICKNESS UNK	OPERATOR	

SPECTRUM NO.
SAMPLE

RECORDING CHARTS

Figure 12. IR Spectrogram (Run 29)



SPECTRUM NO.	**ORIGIN**	**LEGEND**	**REMARKS**
SAMPLE PCDE		**1.**	[illegible]
FROM G. [illegible]	**PURITY** UNK	**2.**	PLATE (FROM CH₂Cl₂ SOLN)
	PHASE LIQUID (VISCOUS)	**DATE** 2 JUNE 75	
	THICKNESS UNK	**OPERATOR**	

SPECTRUM NO.
SAMPLE

Form 610-C-161 Rev 9-65

Figure 13. IR Spectrogram

Results from the difluoramination tests were reviewed. The incomplete difluoramination of the DEPECH was believed to be due to the low concentration of N_2F_4 in the solvent as a result of its poor solubility. Dissociation of N_2F_4 into NF_2 radicals was limited by the reaction temperature which, in turn, was limited by the boiling points of the solvents. The increase in carbonyl content in the reaction products was believed to be associated with hydrolysis and possibly depolymerization of DEPECH. Carbonyl is normally found in PBEP in much smaller amounts. According to E. E. Ryder (private communication) the IR absorbance of carbonyl ($A_{5.8\mu}$) is ratioed to the absorbance of the -CH($A_{3.4\mu}$) as an index of quality and the ratio $A_{5.8\mu}/A_{3.4\mu}$ was found to be <1/3 in good quality PBEP.

The IR absorbances of the DEPECH reaction products for selected functional groups are summarized in Table 7. All of the $A_{5.8\mu}/A_{3.4\mu}$ ratios for the products difluoraminated in acetonitrile are 1.0 or greater. The low molecular weights of PCDE from Runs 29 and 31 are believed to be due primarily to the low molecular weights of the crude PBEP used. The molecular weights of the PBEP crudes were not determined.

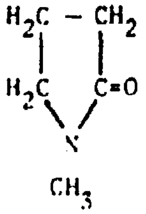
Apparatus and procedures were modified to permit addition of the DEPECH solution to solvent saturated with N_2F_4. All subsequent tests were planned to provide excess N_2F_4 in the reactor.

The first attempt to difluoraminate DEPECH using the modified equipment and procedures (Run 32) was made at 60 C using acetonitrile as the solvent. An addition funnel installed in the apparatus above the reactor as shown in Fig. 4, was charged with 25 ml of DEPECH solution (5.25 wt %) in acetonitrile. The reactor was charged with 50 ml of acetonitrile, purged with helium to remove air, then saturated with N_2F_4 before adding the DEPECH solution slowly. Tetrafluorohydrazine flow was continued throughout the run. The reaction product showed strong IR absorbance at the carbonyl band (5.8 microns) with practically no unsaturation (6.2 microns). The $A_{5.8\mu}/A_{3.4\mu}$ ratio remained very high (2.0).

TABLE 7. INFRARED ABSORBANCE OF DEPECH REACTION PRODUCTS FOR SELECTED FUNCTIONAL GROUPS

Wavelength, microns	2.95	3.45	4.45	5.8	6.0-6.2	11.3	$A_{5.8}/A_{3.4}$
Functional Group	-OH	-CH	-C≡N	-C=O	-C=C-	$-NF_2$	
Run							
15	.03	.28	Trace	.43	.12	.20	1.5
16	.09	.46		.65	.50	.22	1.4
17	.33	.44	Trace	.72	.24	.23	1.6
18	Excessive NO, no DEPECH charged.						
19	.11	.24		.54	.12	.22	2.3
20	.07	.37		.48	.32	.27	1.3
21	.10	.41	.04	.43	.49	.27	1.0
22	.17	.65	.04	.90	.43	.52	1.4
23	.06	.39	.03	.43	.30	.37	1.1
24	.11	.37	.04	.59	.18	.33	1.6
25	.11	.25	.03	.44	.13	.27	1.8
26	.10	.25	.01	.40	.13	.20	1.6
27	.23	.32		.52	.12	.17	1.6
28	.10	.41		.54	.29	.35	1.3
30	.35	.40		.58	.22	.26	1.5
32	.36	.41		.80	.15	.28	2.0
33	.06	.23	.02	.50	.53	.05	2.2
34	.08	.27	.03	.25	.69	.15	0.9
35	.04	.25		.40	.44	.05	1.6
36	.09	.30	.02	.60	.84	.18	2.0
37	.10	.32	.03	.37	.71	.15	1.2
38	.10	.29		.49	.47	.37	1.7
39	.03	.26		.72	.41	.18	2.8
40	.13	.25		.54	.11	.31	2.2
41	.17	.25		.52	.14	.29	2.1
42	.17	.32		.56	.14	.41	1.8
43	.09	.31		.41	.23	.43	1.3
44	.07	.24		.32	.16	.32	1.3
45	.19	.28		.47	.11	.51	1.7

Discovery that N-methyl-2-pyrrolidone was an excellent solvent for DEPECH led to a series of tests to evaluate it as reaction media for difluoraminating DEPECH with N_2F_4. The methyl pyrrolidone has a high boiling point, 202 C, is completely miscible with water and most organic solvents, and has the following structure:



Preliminary solubility tests with DEPECH showed that solution concentrations of 17 wt % are mobile liquids at 20 C, 20 wt % are thixotropic at 25 C, and solutions up to 40 wt % are liquid at 60 C. Dissolved DEPECH recovered from solution had an IR spectrogram identical with the starting material. The stability of N-methyl-2-pyrrolidone in the presence of N_2F_4 was found to be equal or better than acetonitrile as judged by the off-gases observed by gas chromatography when N_2F_4 is passed through the solvent at reaction temperatures. Subsequent experience with 20 wt % solutions of DEPECH in N-methyl-2-pyrrolidone showed considerable variation in gel formation. This is believed to be due to variation in molecular weight of the DEPECH when the small samples are weighed for each reaction. The sample of DEPECH supplied to Rocketdyne does not physically appear to be a homogeneous product.

Difluoramination of DEPECH has been studied using N-methyl-2-pyrrolidone as the DEPECH solvent. The reactions were conducted in methyl pyrrolidone, methyl pyrrolidone-Freon 113 mixture, Freon 112, and with AIBN catalyst in methyl pyrrolidone solution of DEPECH. Test conditions are summarized in Table 5. Apparatus shown in Fig. 4 was used with the following general procedures for Runs 33 through 38. The reactor bath was brought to test temperature and the addition funnel jacket temperature to 40 C. Forty milliliters of solvent were placed in the reactor and 15 ml of 20 wt % DEPECH solution in N-methyl-2-pyrrolidone placed in the closed addition funnel. The apparatus and solvent were purged with helium. With the helium purge off, N_2F_4 flow was started.

The solvent in the reactor was saturated with N_2F_4 before feed of the DEPECH solution from the addition funnel was started. The DEPECH feed solution was added slowly with continuous addition of N_2F_4 in all runs except Run 36. The DEPECH solution was inadvertently added rapidly as a single slug in Run 36 due to pluggage and sudden release in feed line.

The reaction products were recovered from the N-methyl-2-pyrrolidone reaction mixtures of Runs 33, 34, 36, and 37 by adding methylene chloride to the solution and removing the N-methyl-2-pyrrolidone by washing with water. The washed methylene chloride solution was stripped of solvent under nitrogen at room temperature. In Run 35 the methyl pyrrolidone was washed from the Freon 113 solution with water and the Freon stripped off under nitrogen at room temperature. In Run 38 both solvents were stripped off the reaction mixture at 40 C under nitrogen wash.

A silicone rubber septum was added to the head of the reactor and the addition funnel eliminated for Run 39 to avoid feed line pluggage problems encountered in the earlier tests and to provide a more accurate weight of solution delivered. The quantity of DEPECH charged was reduced to lower the DEPECH concentration in the reaction mixture. The DEPECH solution was injected manually through the septum with an all-glass syringe fitted with valve and stainless steel needle. The Freon 112 in the reactor was saturated at 28 C with N_2F_4, the methyl pyrrolidone solution of DEPECH added, the reactor temperature raised to 80 C and held. The flow of N_2F_4 continued throughout the run. The reaction product was recovered directly from the reaction mixture by stripping the solvents at 40 C under gaseous nitrogen wash. The results from fluorine and nitrogen analyses of reaction products of N_2F_4 with DEPECH in N-methyl-2-pyrrolidone and Freon 112 (Runs 36, 37, and 38) are shown in Table 6, the fluorine-to-nitrogen ratio is low in all three. The product from Run 36, where the difluoramination was carried out at 80 C in N-methyl-2-pyrrolidone, showed the lowest F-to-N ratio. Slightly higher F/N ratio was obtained in the product from Run 37 in the same solvent where AIBN (α,α'azo-di-isobutyronitrile) catalyst was used at 70 C. Even better F/N ratio was achieved in Run 38 where part of the N-methyl-2-pyrrolidone was replaced with Freon 112.

These low F/N ratios suggest that N-methyl-2-pyrrolidone slows the difluoramination and possibly adds to or complexes with the DEPECH. The absence of the nitrile band (4.4μ) in the infrared spectra indicates that no dehydrofluorination had occurred, which might also have accounted for the low F/N ratio.

Quantitative product recoveries are shown in Table 8, and IR absorbance for the reaction products given in Table 7.

Results show that difluoramination remained incomplete. This is believed to be due primarily to the limited solubility of N_2F_4 in the solvent at the test conditions. At the lower temperatures, particularly Run 35, the reduced dissociation of N_2F_4 also impeded difluoramination. The addition of AIBN (Runs 34 and 37) appeared to reduce the carbonyl (IR absorbance at 5.8 microns) content slightly but had little effect on difluoramination (as judged by loss of unsaturation, IR absorbance at 6.2 microns). Freon 113 and Freon 112 have been used with N-methyl-2-pyrrolidone in an attempt to increase the solubility of N_2F_4 in the reaction mixture. The mixture of N-methyl-2-pyrrolidone and Freon 113, $F_2ClC\text{-}CCl_2F$, limited the reaction temperature to 55 C (Run 35) due to the low boiling point (47.6 C) of Freon 113. Freon 112 has been used at 70 C (Run 38) and at 80 C (Run 39).

A series of simple solubility tests were made to compare the solubility of N_2F_4 in the various solvents. A search of available literature provided no solubility information for N_2F_4 in acetonitrile, N-methyl-2-pyrrolidone, Freon 112 or Halocarbon oil. Solvent (2 cc) was introduced into an all-glass 10 cc syringe fitted with a valve and a 25-gage stainless-steel needle. The syringe was then filled as rapidly as possible with N_2F_4 at atmospheric pressure to bring the total volume to 10 cc and the valve closed. The syringe was shaken and allowed to come to equilibrium before reading the final volume. These crude tests indicated the relative order of solubility of N_2F_4 in the various solvents were Halocarbon oil 11-21S>Freon 113>Freon 112>acetonitrile>N-methyl-2-pyrrolidone. The Halocarbon oil became turbid as the N_2F_4 dissolved. The order of solubility of DEPECH in the same solvents is the inverse of that for N_2F_4 solubility.

TABLE [illegible]. PRODUCT RECOVERY SUMMARY

Run	DEPECH Charge, gms	Product gms	Weight Ratio	Wt. Gain By Reaction, gm	Weight Gain (gms), Theoretical	Weight Gain % of Theory	Wt. N_2F_4 Used, gms
33	3.15	4.33	1.37	1.18	4.91	24	
34	3.15	4.29	1.23	1.14	4.91	23	
35	3.15	3.30	1.05	0.15	4.91	3	
36	3.05	5.02	1.65	1.97	4.76	41	
37	3.14	4.86	1.55	1.72	4.90	35	
38	3.13	4.63	1.48	1.50	4.88	31	
39	0.777	1.373	1.77	0.596	1.212	49	
40	0.392	0.502	1.28	0.110	0.611	18	
41	0.385	0.541	1.41	0.156	0.601	26	.155
42	0.354	0.540	1.53	0.186	0.552	34	.188
43	0.377	0.634	1.68	0.257	0.588	44	(1)
44	0.397	0.674	1.70	0.277	0.619	45	(1)
45	0.366	0.614	1.68	0.248	0.571	43	.254

---

(1) Not estimated because of apparent reaction with Freon 112.

The test apparatus was rebuilt to permit test operations at pressures up to approximately 10 psig in a closed reaction vessel as shown in Fig. 6. A very small volume pressure transducer has been used in the system to minimize solvent condensation in the gage and lines. The sample ports were silicone rubber diaphragms (septums) mounted in all-Teflon fittings. All-glass syringes fitted with valves and stainless-steel needles were used for taking gas samples at both ports and for injecting solvents or reaction mixtures into the reactor at port No. 2. The reactor system had a total volume of 320 ml. Six difluoramination reactions were made in the closed reactor. The first five (Runs 40 through 44) used acetonitrile as solvent for the DEPECH. The reactor was charged with 30 ml of solvent and the chamber filled with N_2F_4 at approximately 9 psig and allowed to come to equilibrium at reaction temperature with strong agitation of the solvent. The pressure and temperature in the reactor were monitored and recorded until no further pressure decrease was observed.

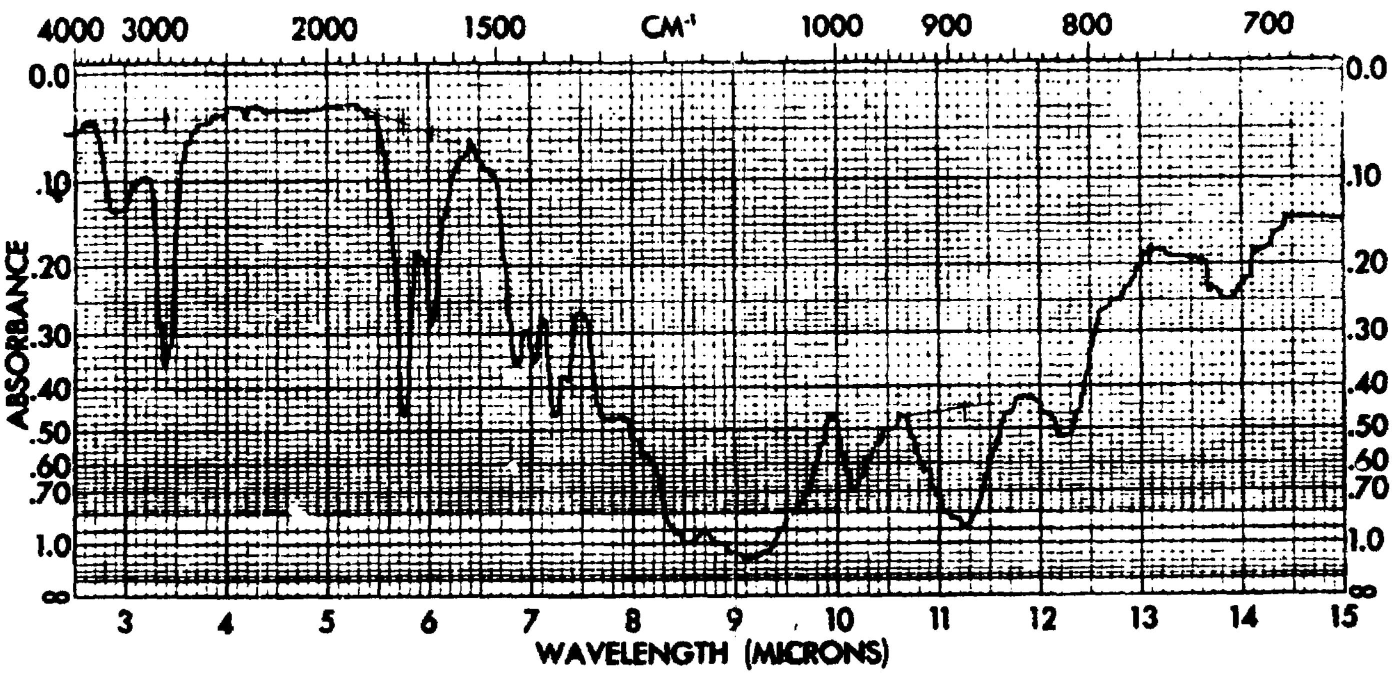
The amount of N_2F_4 charged and consumed were calculated from the PVT data. All runs were made at 70 C. Test conditions for all of the tests are summarized in Table 5. Aceonitrile was used as the reactor solvent in Runs 40, 41, and 42. Run 41 was a repeat of Run 40. Part of the chamber gas was lost during injection of the DEPECH solution into the reactor in Run 40. The catalyst AIBN was added to Run 42. Two runs (43 and 44) were made using Freon 112 as the solvent. It was discovered in Run 43 that unknown gases were evolved when Freon 112 was mixed with N_2F_4. These unidentified gases had not been detected using the Poropak-Q GLC column. The procedure was varied in Run 44 to permit determination of the vapor pressure of the mixed solvents in the presence of DEPECH. The Freon 112, and then the acetonitrile solution of DEPECH, were injected in the evacuated reactor at 30 C and the temperature raised slowly. Pressure and temperature were monitored and recorded. With the system stabilized at 70 C N_2F_4 was added to the reactor as rapidly as possible to 9 psig. Pressure was monitored and recorded until pressure drop ceased. Chamber pressure increase was observed in both runs when N_2F_4 was charged to the reactor containing Freon 112. Methyl ethyl ketone was used as both DEPECH solvent and reactor solvent in Run 45. At the completion of each run, the solvent was stripped off of the reaction products in the reactor at 70 C by venting the reactor to a water aspirator. The stripped product was washed quantitatively into a tared vial with CH_2Cl_2, restripped of solvent under nitrogen at room temperature, and weighed.

The amount of difluoramination in the closed reactor was found to be approximately the same as found using the vented continuous flow reactor as judged by the product weight gain (Table 8). in tests where the N_2F_4 consumption was measured (Runs 41, 42, and 45) the weight of N_2F_4 consumed is in close agreement with the reaction product gain in weight. No analysis for F and N was made since the NF_2 content in earlier reaction products was found to correlate with weight gain of the DEPFCH.

The IR spectra from all of the reaction products prepared in the closed reactor are similar to those from products prepared in the vented continuous flow apparatus. Strong carbonyl (5.8 microns) absorption bands appear in all. The IR spectra for Runs 43 (Fig. 14) and Run 44 (Fig. 15) are typical. Retention of appreciable amounts of unsaturation (6.2-micron band) in Runs 43 and 44 while adding a slightly greater amount of weight suggests that the unsaturated bonds may have undergone fewer side reactions. The N_2F_4 consumption for these runs could not be calculated to corroborate the weight gain measured due to unknown, inert gas evolution. It is possible that some residual solvent (Freon 112) may have been retained.

The solubility of N_2F_4 in CH_3CN measured in the closed reactor was found to be 0.0015 g/ml at 70 C and 0.013 g/ml at 25 C. Estimate of the solubility of N_2F_4 in Freon 112 was not possible due to evolution of unknown gases.

A separate test was made to estimate the quantity of gas evolved by the N_2F_4-Freon 112 mixture. An additional 0.0013 mole of gas were generated at 70 C when 0.010 mole of N_2F_4 was added to the reactor containing 20 ml of Freon 112.

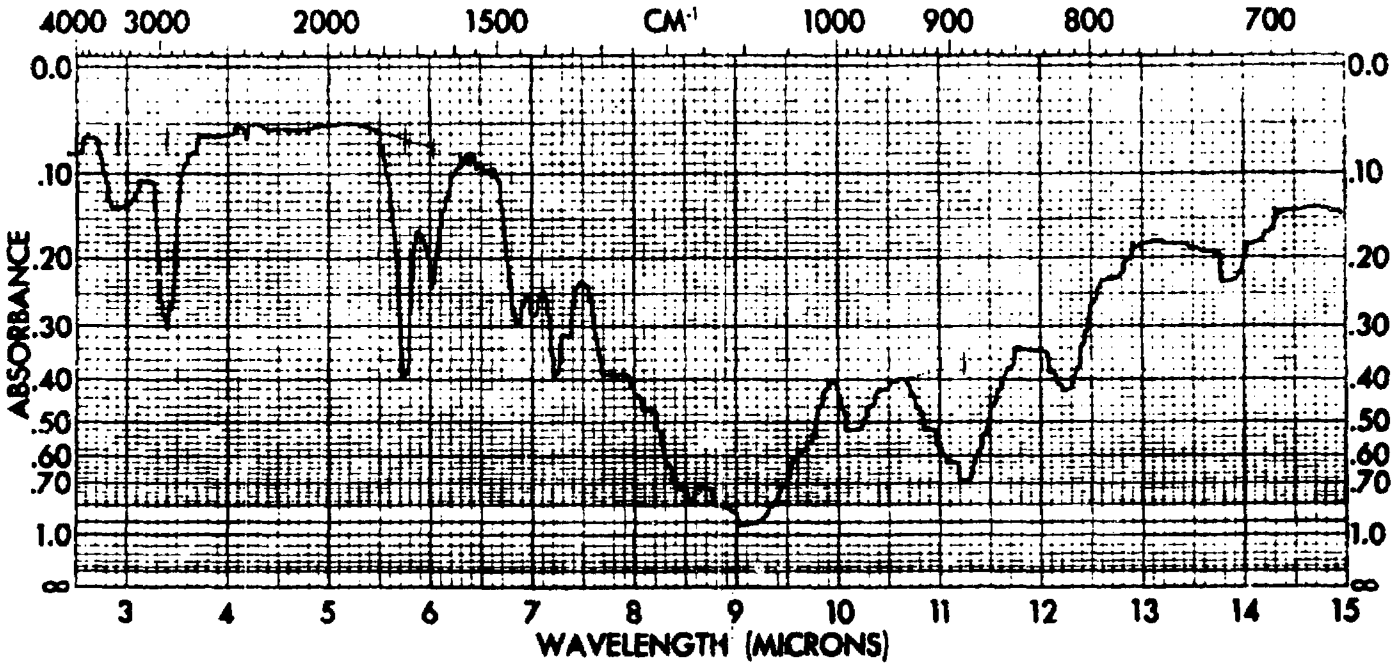


SPECTRUM NO.______
SAMPLE ______

SPECTRUM NO.	ORIGIN	LEGEND	REMARKS Film on NaCl plate from CH_2Cl_2 sol'n
SAMPLE Reaction Product Difluoramination of DEPECH in mixed solvents (Freon 112 + CH_3CN) at 70°C		1.	
	PURITY unk	2.	
Run 43	PHASE Liquid (viscous)	DATE 23 Jan '76	
	THICKNESS ~ 1 mil	OPERATOR C. L. West	

Form 610-C-161 Rev 9-65

Figure 14. IR Spectrogram (Run 43)



SPECTRUM NO.

SAMPLE REACTION PRODUCT DIFLUORAMINATION OF DEPE-N WITH N$_2$F$_4$ IN MIXED SOLVENTS ~~(FREON 11 & CH$_3$CN AT 70°C)~~

RUN 44

ORIGIN

PURITY

PHASE LIQUID

THICKNESS ~1 MIL

LEGEND

1.

2.

DATE 26 JAN '76

OPERATOR C. L. West

REMARKS

FILM ON NaCl PLATE FROM CH$_2$Cl$_2$ SOL'N

SPECTRUM NO.

SAMPLE

Form 610-C-161 Nov 9-65

Figure 15. IR Spectrogram (Run 44)

RECOMMENDATIONS

All the solvents studied during the progress of the work showed either good N_2F_4 solubility and poor ability to dissolve DEPECH or the reverse. However, continued search is recommended for a solvent or solvent mixtures in which both N_2F_4 and DEPECH are mutually soluble. To operate at pressures near ambient, the solvents must have relatively high boiling points to avoid excessive vapor pressures at temperatures high enough (>60 C) to dissociate N_2F_4 into NF_2 radicals.

Radical initiators more active than AIBN should be investigated to determine whether N_2F_4 could be dissociated at lower temperatures for reaction with DEPECH which could possibly minimize carbonyl formation.

REFERENCES

1. Fetterly, L. C., A. C. Mueller, J. C. Rapeau, E. C. Ryder, E. L. Capener, and J. G. Berke, *Establish Manufacturing Process for Energetic Propellant Binder*, Shell Development Co., Technical Report AFML-TR-71-56, May 1971.

2. Hurst, G. L. and S. I. Khayat, *Investigation of the Existence of Oxyanions of Fluorine and Nitrogen and the Nitrogen-Fluorine Cations*, Harshaw Chemical Co., Report HQ-76-10, 28 August 1965.

3. *Research on Advanced Solid Propellants*, Esso Res. and Eng. Co., QPR-1, Contract DA-30-069-ORD-2487, 30 June 1959.

4. Olin Matheson, Final Report NH-1552-SSD-TR-61-30, Vol. 1, Part I., Contract AF-33(616)-6785, December 1960.

5. Petry, R. C., J. P. Freeman, C. O. Parker, T. E. Stevens, and S. R. Reed, First JANNAF Meeting, Liquid Propellant Group, New Orleans, La., Vol. II, November 1959.

6. Craig, A. D. et al., *A Study of the Electronic Configuration and Behavior of the NF_2 Group*, Hercules Powder Co., Report HRC-64-3, 25 June 1964.