

UNCLASSIFIED

AD NUMBER

AD039245

CLASSIFICATION CHANGES

TO: unclassified

FROM: confidential

LIMITATION CHANGES

TO:  
Approved for public release; distribution is unlimited.

FROM:  
Distribution authorized to U.S. Gov't. agencies and their contractors;  
Administrative/Operational Use; APR 1954. Other requests shall be referred to Office of Naval Research, Washington, DC.

AUTHORITY

Tab U61-2-5, 1 Jun 1961; onr ltr, 10 apr 1961

THIS REPORT HAS BEEN DELIMITED  
AND CLEARED FOR PUBLIC RELEASE  
UNDER DOD DIRECTIVE 5200.20 AND  
NO RESTRICTIONS ARE IMPOSED UPON  
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED.

UNCLASSIFIED

---

AD 39245

*Reproduced  
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY  
ARLINGTON HALL STATION  
ARLINGTON 12, VIRGINIA



DECLASSIFIED  
PER AUTHORITY  
TAB *461-2-5*  
DATED *JUNE 61*

---

UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CNR NITROPOLYMER RESEARCH  
Contract Nonr-1205(00)

January 1, 1954 to  
March 31, 1954

Copy No. 25

Report No. C-9

CONFIDENTIAL

COMMERCIAL SOLVENTS CORPORATION

TERRE HAUTE, INDIANA

TELEPHONE CRAWFORD 7071

IN REPLY REFER TO -

April 5, 1954  
Copy No. 25

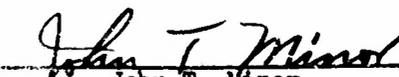
Report No. Q-9  
(Quarterly Summary)

SUBJECT: ONR Nitropolymer Research

CONTRACT: Nonr-1205(00)

PERIOD COVERED January 1, 1954 to  
March 31, 1954

WRITTEN BY:

  
John T. Minor  
Chief Investigator

APPROVED BY:

  
Jerome Martin  
Director of Research

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

CONFIDENTIAL

34 AA

56155

TABLE OF CONTENTS

	<u>Page</u>
Contract Fulfillment	iii
I. SUMMARY . . . . .	1
II. TECHNICAL PROGRESS . . . . .	1
A. Introduction . . . . .	1
B. Acrylyl Chloride . . . . .	2
C. 2,2-Dinitropropyl Acrylate . . . . .	2
D. 2,2-Dinitropropanol . . . . .	2

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-9

CONTRACT FULFILLMENT

This quarterly report is submitted in partial fulfillment of  
Contract Nonr-1205(00).

CONFIDENTIAL

I. SUMMARY

A. This quarterly report is the third under Contract Nonr-1205(00) and covers the period from January 1, 1954 to March 31, 1954. The object of the contract is: Conduct research in the synthesis of polynitro compounds to include, but not necessarily be limited to, a review of the chemistry and the processes of preparation of the more useful products of research from the nitropolymer program and investigate the applications of processes not now employed in the preparations.

B. The more important results and conclusions of the work of the quarter are presented below.

1. Of the methods for preparing acrylyl chloride, that using acrylic acid and benzoyl chloride appears to be the most feasible.

2. The dinitropropyl acrylate process might be improved slightly by adding the aluminum chloride to the mixture of dinitropropanol and acrylyl chloride.

3. Silver nitrate recovery in the Shechter-Kaplan reaction will be good if all mechanical loss is avoided. This is true only if the unreacted silver ions are recovered from the reaction solution, preferably by strong base.

4. In the preparation of dinitropropanol by the Shechter-Kaplan reaction, there is little effect on yield from wide ranges of reaction temperature or time.

II. TECHNICAL PROGRESSA. INTRODUCTION

The principal effort during the quarter has been to review the processes leading to poly dinitropropyl acrylate. This effort led to a re-examination of the processes available for the preparation of acrylyl chloride, dinitropropanol, and dinitropropyl acrylate.

B. ACRYLYL CHLORIDE (AC)

As reducing the cost of AC appears to be the most promising point to start for reducing the cost of DNPA, the processes by which AC can be made were reviewed briefly. A comparison of several procedures was made by C. H. Stempel et al (1) and the reaction of benzoyl chloride with acrylic acid was favored over that of acrylic acid with thionyl chloride, phosphorus oxychloride, phosphorus trichloride, or phosphorus pentachloride. Attempts to repeat their work fell short of obtaining the reported yield of 68-72% by about 15%.

Two other procedures which can be handled in the laboratory, namely from  $\beta$ -propiolactone through  $\beta$ -chloropropionyl chloride (2), and from sodium acrylate with phosphorus oxychloride (3), present handling and hazard difficulties which decrease their ease of scale-up.

A British patent (4) presents a process of passing chlorine and acrolein through a hot quartz tube and reports giving a "good yield". It is an interesting potential process but no laboratory work is contemplated at this time.

Due to the percentage of chlorine present in benzotrichloride, it appears to be an economical chlorinating agent. When it was used, a 37% yield of redistilled acrylyl chloride was obtained. The reaction was run in 100 grams of Dowtherm using 1.0 mole of acrylic acid and 0.50 mole of benzotrichloride. Two similar runs were made without a solvent and as soon as the reaction mixture reached 60-70°C, polymerization set in.

As benzoyl chloride and acrylic acid are both commercially available and the process utilizing these starting materials presents fewer production problems, it would be favored at this time for the preparation of AC.

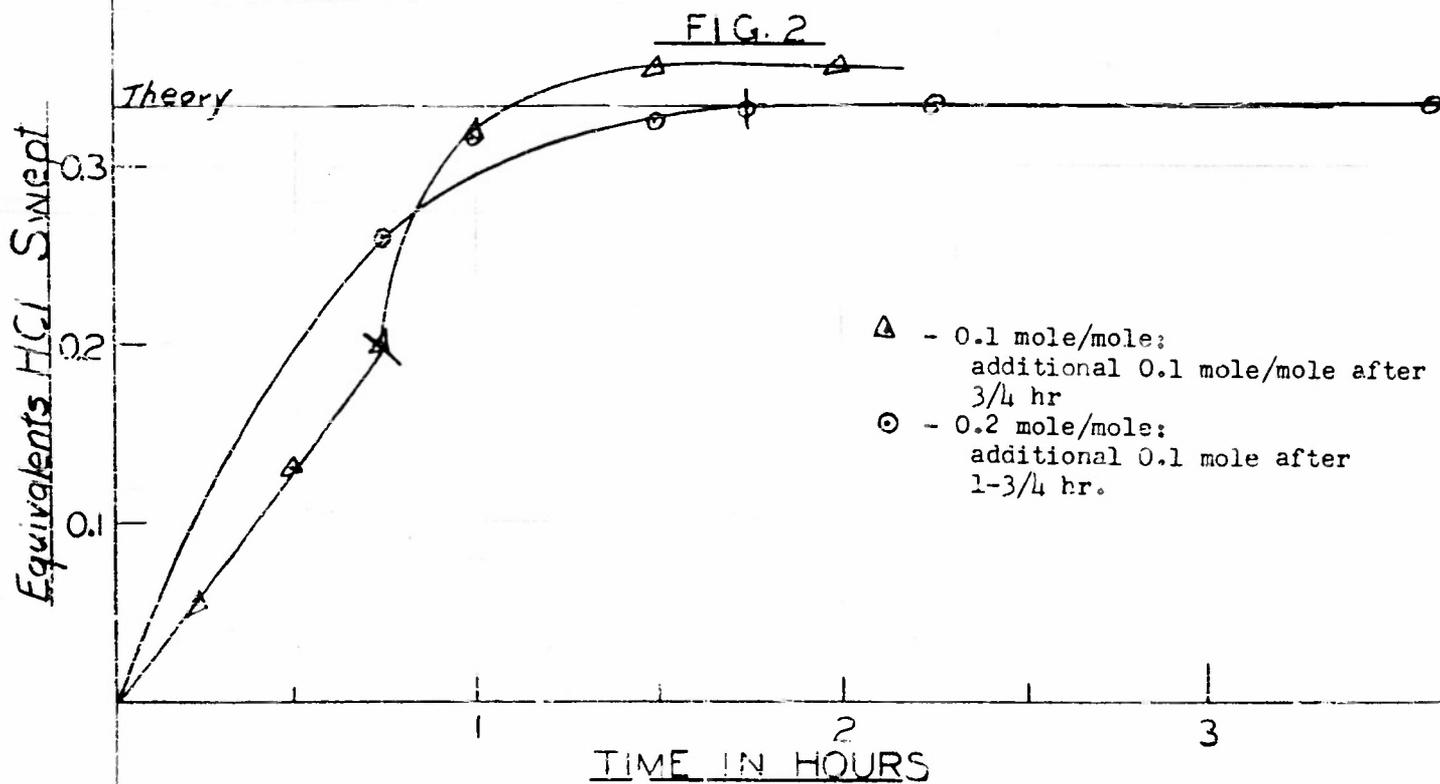
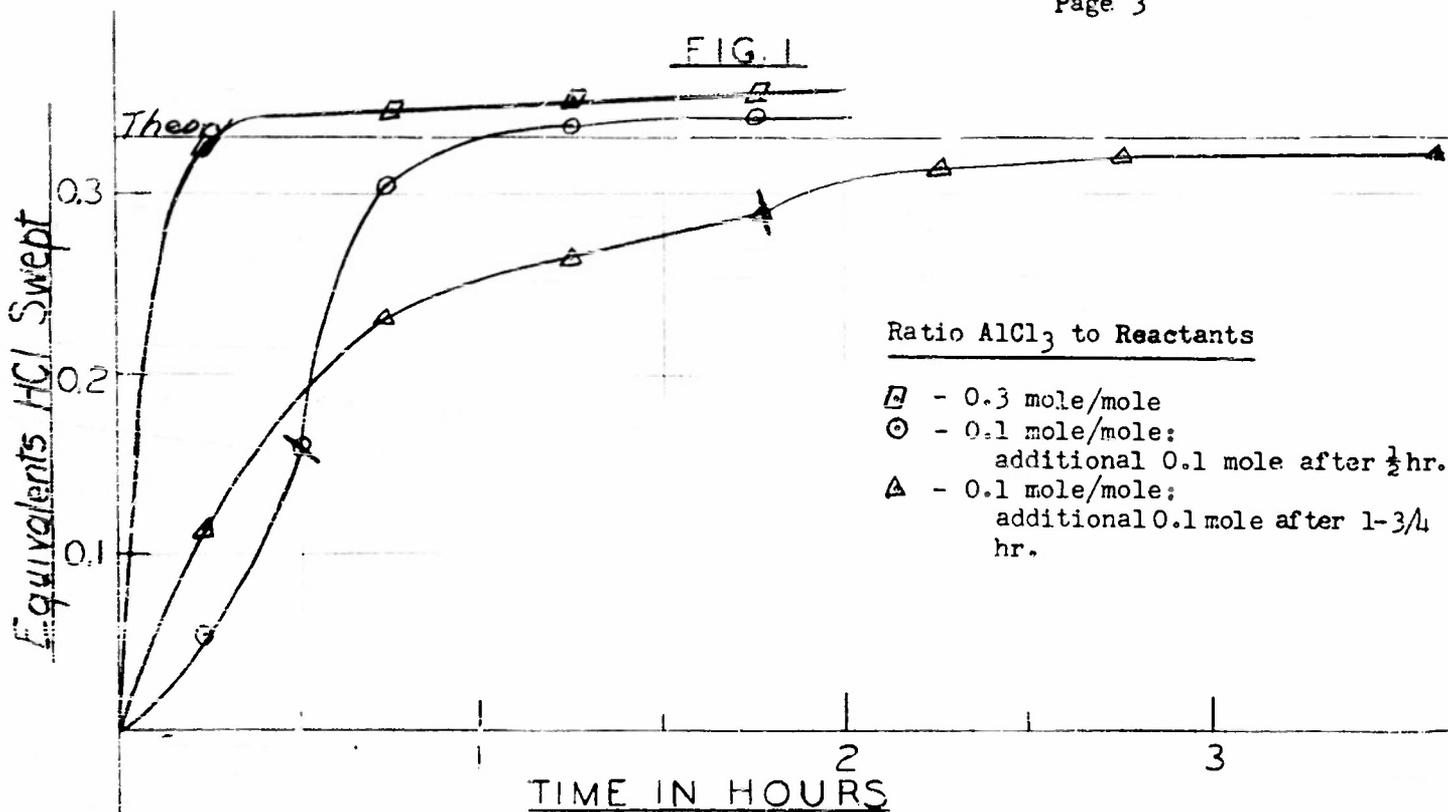
#### C. DINITROPROPYL ACRYLATE (DNPA)

Since the preparation of DNPA in several runs in our pilot plant study was erratic in respect to yield (5) we have reviewed the process in an attempt to eliminate some loss. In the process as used, the aluminum chloride was added to the dinitropropanol (DPL) solution and the temperature raised to 45°C, followed by the addition of the acrylyl chloride (AC) solution. It was suggested (6) that since the complex formed between aluminum chloride and DPL promotes decomposition on prolonged heating it might be better to add the aluminum chloride to the AC solution. Attempts to do this resulted in lower yields and a darker colored product. As the aluminum chloride is detrimental to both reactants it was concluded that this should be the last material to be added to the reaction. Runs have been made in which the aluminum chloride was added to the solution of AC and DPL in ethylene dichloride, initially at room temperature. Some rate data were obtained with various ratios of catalyst as shown in Figures 1 and 2. These figures plot the hydrogen chloride liberated and swept from the reaction flask into standard base against time. Results indicate that a 0.20 mole quantity of aluminum per mole of reactants is sufficient to give a complete reaction in 1-3/4 hours at 50°C. This procedure improves the color of the final product slightly and yields compare favorably to those for the original process.

In an attempt to find a purification procedure that eliminated the many washings where our loss of product was high, steam distillation was again tried. The reaction mixture can be steam distilled directly to remove the solvent and the DNPA. However the amount of steam required is high, at least 30 lbs. per lb. of product, and recoveries are not complete. Steam distillation at reduced pressure was not appreciably different from that at normal pressure. It would be very desirable to isolate the product in this manner as loss and labor could be reduced; however, it is not recommended as a process at this time.

#### D. DINITROPROPANOL (DPL)

If the cost of acrylyl chloride can be reduced considerably, or an esterification process developed in which acrylic acid is used, the major cost item in DNPA production would then be DPL. We have reexamined the process used in its preparation to see if it is possible to lower the silver nitrate loss, increase yield, and to determine the limits of the process conditions. Table I summarizes this work using DPL and 2,2-dinitropropanediol as reaction products. These data show that the major quantity of the silver not reduced in the reaction can be precipitated from the resulting solution by strong base to arrive at an acceptable silver balance.



It would seem that the conditions of the process for the preparation do have a wide latitude. As noted in Table I, there is only slight variation in yield when the salt solution is added as a unit, added dropwise over a one hour period, or added and let stand 18 hours before filtering. Also, the yield was not appreciably lowered when no cooling was used as compared to that when the temperature was not allowed above 30°C. There was however some variation in the ratio of silver precipitated and that remaining in the reaction solution.

It has been found that DPL has a good solubility differential between 70°C and room temperature in monochlorotoluene. Better than a 90% yield of nice DPL crystals was obtained from crude product, pulled dry by means of a vacuum pump, using monochlorotoluene and hexane as a mixed re-crystallization solvent.

Table I

Dinitropropanediol Preparation(a)

Run	Conditions	Yield(b)	AgNO <sub>3</sub> Recovered		
			from Cake	from Raffinate	Total
115	Analytical grade AgNO <sub>3</sub> ; S.P.(c)	72	97.39	1.83	99.22
116	" " " "	lost	96.50	2.20	98.70
117	" " " "	57	97.33	2.20	99.53

Dinitropropanol Preparation(a,d)

121	30 min., 40°C	--	96.94	2.34	99.28
122	S.P.	82	99.40	.30	99.70
123	"	--	97.89	1.57	99.46
124(c)	"	--	98.20	1.63	99.83
126	5 min., 30°C	77	99.71	.52	100.23
128	18 hours, 30°C	87	97.02	2.26	99.28
130	S.P.	89	--	1.35	--
132	10 min., 35°C	89	97.02	3.10	100.12
133	15 min., 42°C	79	--	3.37	--
134	dropwise for 1 hour, 28°C	85	100.28	0.04	100.32
Mean Recovery					99.60

(a) Runs were made on a 0.50 g. mole basis (1.0 g. mole AgNO<sub>3</sub>).

(b) Yield was based on material extracted but not volatile at 75° and 1-2 mm.

(c) S.P. - Standard procedure: Add all of the salt solution to the silver nitrate solution at once, keep temperature below 30°C, and filter after 30 min.

(d) All silver nitrate in this series was the same recrystallized, recovered material.

(e) This run was on a 1.0 g. mole basis.

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-9  
Page 5

REFERENCES

1. C. H. Stempel, R. Cross, and R. Mariella, J. Am. Chem. Soc. 72, 2299 (1950).
2. T. L. Gresham, J. Jansen, and F. Shaver, J. Am. Chem. Soc. 72, 72 (1950).
3. B. F. Goodrich Chemical Co., private communication.
4. British Patent 626,772.
5. Commercial Solvents Reports Q-8, p. 2.
6. D. V. Sickman, NOL, private communication.

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-9  
Page 6

	<u>No. of Copies</u>		<u>No. of Copies</u>
Dept. of the Air Force Hq. USAF, DCS/D Washington 25, D.C. Attn: AFDRD-AN, Maj. H. R. Schmidt	1	Commanding General Redstone Arsenal Huntsville, Alabama Attn: Technical Library	2
Commanding General Wright Air Development Center Wright-Patterson Air Force Base Ohio Attn: WCEGH-2	1	Department of the Navy Bureau of Aeronautics Washington 25, D.C. Attn: SI-5	1
Commanding General Wright Air Development Center Wright-Patterson Air Force Base Ohio Attn: WCLPN-2	1	Department of the Navy Bureau of Ordnance Washington 25, D.C. Attn: Ad3, Technical Library	1
Commanding General Wright Air Development Center Wright-Patterson Air Force Base Ohio Attn: WCRRC	1	Commanding Officer U.S. Naval Air Rocket Test Station Lake Denmark Dover, New Jersey Attn: Technical Library	1
Commanding General Aberdeen Proving Ground Maryland Attn: Ballistic Research Laboratories ORDBG-BLI	2	Commanding Officer U.S. Naval Powder Factory Indian Head, Maryland Attn: Research and Development Department	2
Commanding General Frankford Arsenal Bridge and Tacony Streets Philadelphia, Pennsylvania Attn: Pitman-Dunn Laboratory	1	Commander U.S. Naval Ordnance Laboratory White Oak Silver Spring, Maryland Attn: Library	1
Department of the Army Office, Chief of Ordnance Washington 25, D. C. Attn: ORDTU	1	Commander U. S. Naval Ordnance Test Station Inyokern, China Lake, California Attn: Technical Library Branch 3	3
Commanding Officer Office of Ordnance Research Box CM Duke Station Durham, North Carolina	1	Department of the Navy Office of Naval Research Washington 25, D.C. Attn: Code 429	3
Commanding Officer Picatinny Arsenal Dover, New Jersey Attn: Library	2	Commanding Officer Office of Naval Research Branch Office 86 East Randolph Street Chicago 1, Illinois Attn: Lt. M. C. Laug	1

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-9  
Page 7

	<u>No. of Copies</u>		<u>No. of Copies</u>
Commanding Officer Office of Naval Research 1030 East Green Street Pasadena 1, California	1	Experiment, Incorporated P. O. Box 1-T Richmond 2, Virginia Attn: Librarian	1
Bureau of Aeronautics Representative c/o Aerojet-General Corporation Azusa, California	1	Hercules Experiment Station Wilmington, Delaware Attn: A. M. Ball	1
Department of the Navy Bureau of Aeronautics Washington 25, D.C. Attn: TD-4	1	Director Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena 3, California	1
Aerojet-General Corporation P. O. Box 296 Azusa, California Attn: Librarian	2	Arthur D. Little, Inc. 30 Memorial Drive Cambridge 42, Massachusetts Attn: W. A. Sawyer	1
Allegany Ballistics Laboratory P. O. Box 210 Cumberland, Maryland	1	Arthur D. Little, Inc. 30 Memorial Drive Cambridge 42, Massachusetts Attn: W. C. Lothrop	1
Armour Research Foundation of Illinois Institute of Technology Technology Center Chicago 16, Illinois Attn: Propulsion and Structures Research; Department M	1	Naval Ordnance Research School of Chemistry University of Minnesota Minneapolis 14, Minnesota Attn: B. L. Crawford, Jr.	1
Atlantic Research Corporation 812 North Fairfax Street Alexandria, Virginia	1	National Fireworks Ordnance Corp. West Hanover, Massachusetts Attn: S. J. Porter	1
Bureau of Mines 4800 Forbes Street Pittsburgh 13, Pennsylvania Attn: Explosives and Physical Sciences Division	2	Ohio State University Research Foundation Columbus 10, Ohio Attn: Harold Shechter	1
Catholic University of America 7th St. and Michigan Ave., N.E. Washington 17, D.C. Attn: F. C. Rice	1	Phillips Petroleum Company Bartlesville, Oklahoma Attn: J. P. Alden	1
E. I. du Pont de Nemours & Co. 10th and Market Streets Wilmington, Delaware Attn: W. F. Jackson	1	Project Squid Princeton University Princeton, New Jersey Attn: Librarian	1

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-9  
Page 8

	<u>No. of Copies</u>		<u>No. of Copies</u>
Purdue University Department of Chemistry Lafayette, Indiana Attn: Henry Feuer	1	B. F. Goodrich Company Research Center Brecksville, Ohio Attn: Vice President/Research	1
Rohm and Haas Company Redstone Arsenal Research Division Huntsville, Alabama Attn: Technical Director	1	Department of the Navy Bureau of Aeronautics Washington 25, D.C. Attn: Aer 12-3 Contents only marked "For British Joint Services Mission"	4
Solid Propellant Information Agency Applied Physics Laboratory The Johns Hopkins University Silver Spring, Maryland Attn: P. K. Reilly, Jr.	8	Department of the Navy Bureau of Aeronautics Washington 25, D. C. Attn: Aer 12-3 Contents only marked "For Canadian Joint Staff"	4
Standard Oil Company Research Department P. O. Box 431 Whiting, Indiana Attn: W. H. Bahlke	1	Department of Chemistry Ohio State University Columbus 10, Ohio Attn: Elizabeth F. Riley	1
Thiokol Chemical Corporation Redstone Arsenal Huntsville, Alabama Attn: Technical Director	2	Explosives Division Naval Ordnance Laboratory White Oak Silver Spring 19, Maryland Attn: D. V. Sickman	1
Thiokol Chemical Corporation Elkton Division Elkton, Maryland Attn: D. W. Kershner	1	California Institute of Technology Pasadena, California Attn: E. R. Buchman	1
U. S. Rubber Company General Laboratories Market and South Streets Passaic, New Jersey Attn: P. O. Tawney	1	General Aniline & Film Corp. Central Research Laboratory Easton, Pennsylvania Attn: Joseph W. Lang	1
Western Cartridge Company East Alton, Illinois Attn: R. L. Womer	1	Department of Chemistry Purdue University Lafayette, Indiana Attn: G. B. Bachman	1
Reaction Motors, Inc. Rockaway, New Jersey Attn: Librarian	1	Bureau of Ordnance, Re2c Department of the Navy Washington 25, D. C. Attn: T. L. Brownyard	1
Phillips Petroleum Company P. O. Box 548 McGregor, Texas Attn: Librarian, J. Wiss	2		

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. O  
Page 2

	<u>No. of Copies</u>		<u>No. of Copies</u>
Department of Chemistry George Washington University Washington, D. C. Attn: William F. Sager	1	Evans Research and Development Corp. 250 East 43rd Street New York 17, New York Attn: E. J. Hewitt	1
Department of Chemistry University of Maryland College Park, Maryland Attn: N. L. Drake	1	Los Alamos Scientific Laboratory Los Alamos, New Mexico Attn: Technical Library	2
Commanding Officer Chemical Corps Chemical and Radiological Laboratories Army Chemical Center, Maryland Attn: Technical Library	1	Ethyl Corporation 1600 West Eight Mile Road Ferndale 20 Detroit, Michigan Attn: Roy Sugimoto	1

CONFIDENTIAL

UNCLASSIFIED

UNCLASSIFIED