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CNR NITROPOLYMER RESEARCH  
Contract Nonr-1205(00)

January 1, 1954 to  
March 31, 1954

Copy No. 25

Report No. Q-9

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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

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CONTRACT FULFILLMENT

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

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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 PROGRESS

A. 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.

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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)

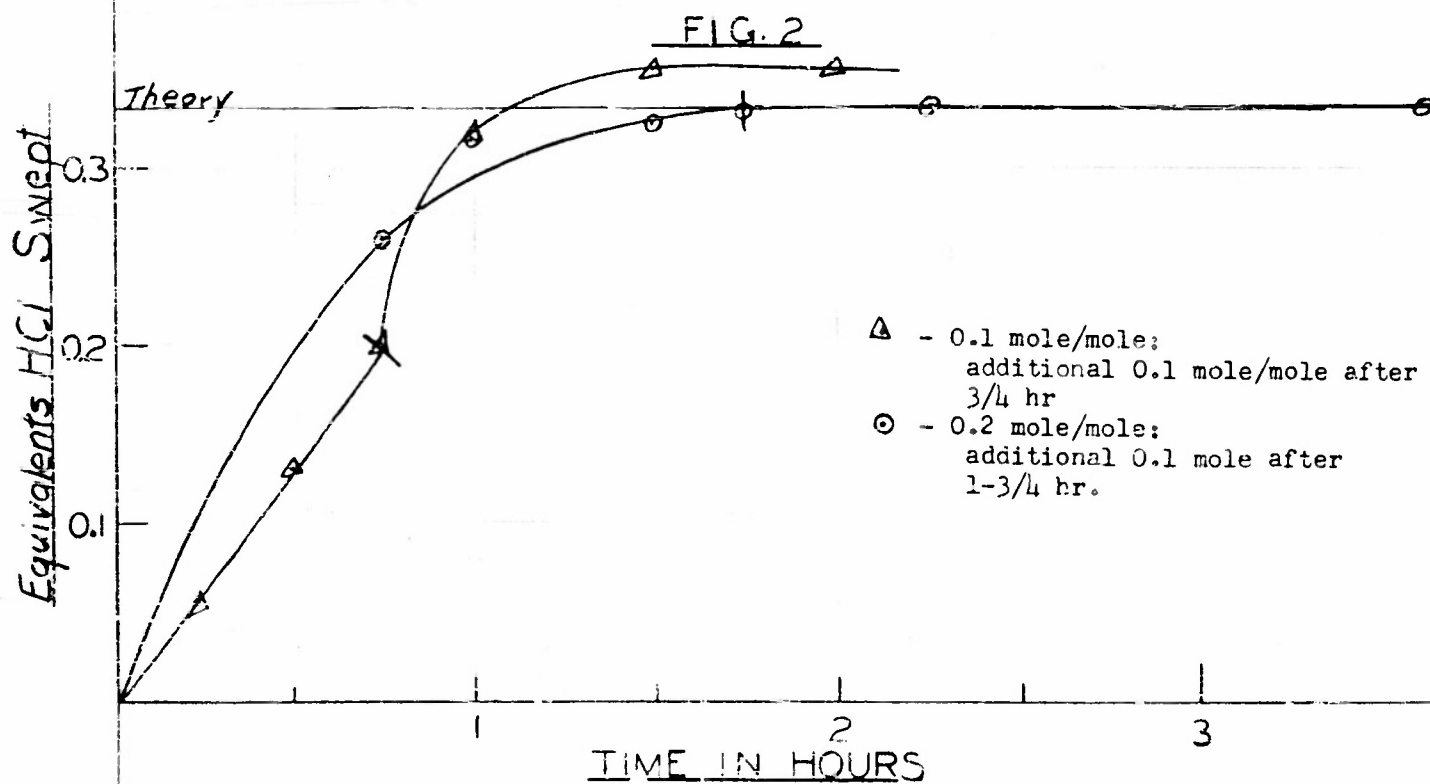
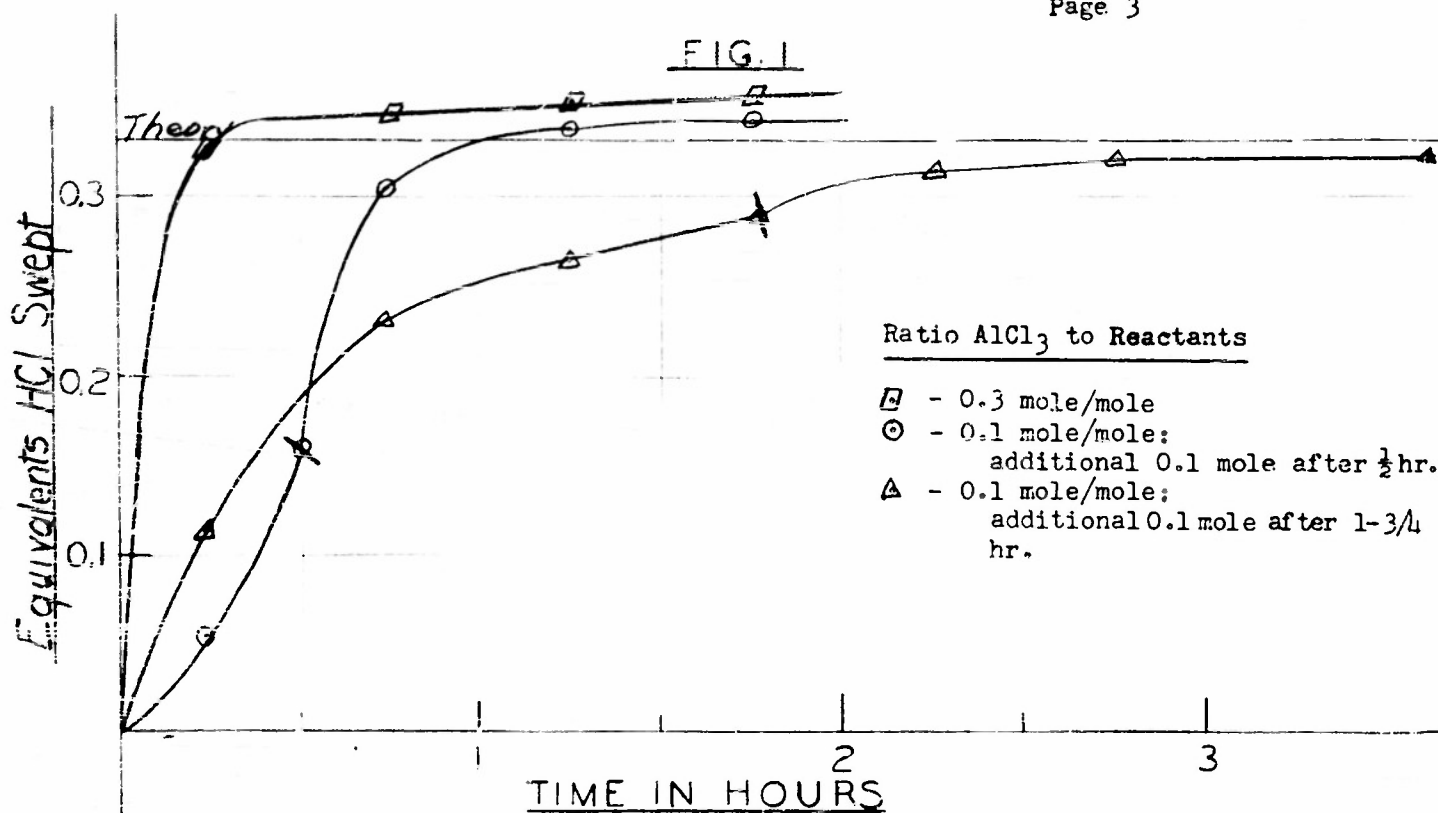
Since the preparation of DNPA in several runs in our pilot plant study was erratic in respect to yield (5) we have reviewed the process in an attempt to eliminate some loss. In the process as used, the aluminum chloride was added to the dinitropropanol (DPL) solution and the temperature raised to 45°C, 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.

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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 recrystallization solvent.

Table I  
Dinitropropanediol Preparation(a)

| Run | Conditions                                   | Yield(b) | AgNO <sub>3</sub> Recovered |                   |       |
|-----|----------------------------------------------|----------|-----------------------------|-------------------|-------|
|     |                                              |          | from<br>Cake                | from<br>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.

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