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ONR NITROPOLYMER RESEARCH
Contract Nonr-1205(00)

April 1 - June 30, 1954

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CONFIDENTIAL

COMMERCIAL SOLVENTS CORPORATION

TERRE HAUTE, INDIANA

TELEPHONE CRAWFORD 7071

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(Quarterly Summary)

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CONTRACT: Nonr-1205(00)

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WRITTEN BY:

John T. Minor
Chief Investigator

APPROVED BY:

Jerome Martin
Director of Research

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COMMERCIAL SOLVENTS CORP. Report No. Q-10

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CONTRACT FULFILLMENT

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

COMMERCIAL SOLVENTS CORP. Report No. Q-10

I. SUMMARY

A. This quarterly report is the fourth under Contract Nonr-1205(00) and covers the period from April 1, 1954 to June 30, 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. Using pilot plant dinitropropanol (DPL), acrylic acid, and poly phosphoric acid in the preparation of dinitropropyl acrylate (DNPA), it is difficult to control premature polymerization.

2. When toluene is used to prepare DNPA from pilot plant DPL and acrylic acid in poly phosphoric acid, trouble is encountered in obtaining good yields of monomer that will mass polymerize to a soluble product.

3. Good yields of 2-nitro-2-nitrosopropane can be prepared using ferric ion instead of silver ion in the oxidative nitration procedure.

II. TECHNICAL PROGRESS

A. DINITROPROPYL ACRYLATE

1. Discussion

We have studied the preparation of dinitropropyl and commercial acrylic acid in a poly phosphoric acid medium. The initial runs were made to check conditions for obtaining good yields. These were far from the 85 and 94% reported (1). The runs in Table I were made with dinitropropanol prepared in the pilot plant except as noted. This material was the same as we had used in preparations using acrylyl chloride to produce DNPA that polymerized to a soluble polymer. Two different samples of poly phosphoric acid were used. From the results of these runs, one would have to conclude that the chances of having esterification in this strong solvent without premature polymerization were small when our pilot plant DPL is used. This observation has been confirmed on a pilot plant scale (1). When toluene or benzene was used to dissolve the DPL and left in or removed from the reaction mixture, little trouble was encountered with polymerization. Also, these data show the difficulty in obtaining a soluble polymer from the monomer as we were able to prepare it.

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1. L. Smith, private communication.

2. Experimental

To 120 g. of poly phosphoric acid in a mechanically stirred flask is added a solution of 75 g. (0.50 mole) dinitropropanol in 30 ml. of toluene. The temperature is raised by steam bath to 60°C, and water pump vacuum pulled until all volatile material is removed. Then 55 g. (0.72 mole) of commercial glacial acrylic acid containing inhibitor is added and the temperature is maintained at 50-60°C. for three hours. The reaction mixture is stirred into water and the oil extracted twice with ether. After washing the combined ether layers successively with water, 2% sodium hydroxide, 4% sodium bisulfite, and water, the ether is removed and the product pulled dry by vacuum to obtain 73.5 g. (72% yield) of DNPA monomer.

TABLE I

Run	DPL	Acrylic Acid	Poly Phosphoric Acid	Toluene	Yield	Polymer by Mass
142	75 g.	48 g.	100 g.		24%	sol.
143	75	45	100		49	no run
146	75	43	100		poly.	
146A	75	43	75		poly.	
147	75 (Re-X)	43	150		35	no run
147A	75 (Re-X)	43	100		20	"
503	70 (Sub)	55	140		35	"
504	75 (Sub)	55	120	75 ml.	66	"
505	75	55	120	25 (removed)	72	"
506	164 (DBL)	110	250		poly.	
507	150	110	250	60	54	no run
508	150	110	250	60	65	Insol.
509	75	55	120		poly.	
510	75	55	120	30 (20 removed)	20 (steam distilled)	
511	150	110	240	30 benzene	50	Insol.
514	150	100	240	30	66	Insol.
		monomer from 514 rewashed				Insol.

B. OXIDIZING AGENTS FOR NITROPARAFFIN SALTS

In our continual search for a reagent that will replace silver ion for the oxidation of the nitroparaffin salts in the presence of nitrite, several systems were tried. One that has been suggested is an oxidizing agent in the presence of silver. Using the sodium salt of 2-nitropropane in the presence of nitrite, one equivalent of silver ion and one equivalent of hydrogen peroxide did not yield any more dinitropropane than if the silver alone had been used. When ferric ion, or the complex ferricyanide, was used under the same conditions as the oxidative-nitration using silver, a 94% yield of 2-nitro-2-nitrosopropane was immediately precipitated.

C. DINITROBUTYL ACRYLATE

Dinitrobutanol was prepared in the standard oxidative-nitration procedure from fractionated 1-nitropropane in 81 and 87% yields. In one preparation after the precipitated silver had been washed twice, by slurring and filtering, and dissolved in nitric acid, an oil layer appeared. The layer was separated, washed, and distilled to obtain 40 g. of colorless product identified by nitrogen analysis and refractive index as dinitrobutanol. This amounts to 8.5% of the theoretical product and indicates the difficulty of washing the cake completely.

Dinitrobutyl acrylate was prepared by the acrylyl chloride-aluminum chloride procedure in 70 and 81% yields. The first run produced an insoluble polymer on bulk polymerization.

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