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COMMERCIAL SOLVENTS CORPORATION

36856

TERRE HAUTE, INDIANA

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July 5, 1953

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FINAL REPORT

ONR NITROPOLYMER RESEARCH
Contract Nonr-397(00)
by

John T. Minor

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Approved:

Jerome Martin
Jerome Martin
Director of Research

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CONTRACT FULFILLMENT

This final report is submitted in partial fulfillment of
Contract Nonr-397(00).

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I. SUMMARY

A. OBJECT OF THE CONTRACT

This final report under Contract Nonr-397(00) covers the material presented in quarterly reports Q-1, Q-2, Q-3, Q-4, Q-5, and Q-6. The period covered was October 15, 1951 to June 30, 1953. The object of Contract Nonr-397(00) was as follows: Shall 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 application of processes not now employed in the preparations. The program was directed towards the industrial development of nitropolymer starting materials and intermediates and the evaluation, both economically and practically, of their processes in the pilot plant. Pilot plant runs were made on several compounds.

B. ABSTRACT

1. 2-Nitroethanol has been prepared from nitromethane and formaldehyde in a column reactor, adaptable to continuous production, in 66% yield.
2. 2-Nitro-1,3-propanediol can be prepared from nitromethane and formaldehyde with the exclusion of nitroethanol or tris(hydroxymethyl)-nitromethane. The product is best extracted using a countercurrent extraction column with butanol solvent and recrystallization of the product from diethyl ether. The butanol extract can be reduced to prepare 2-amino-1,3-propanediol.
3. The preparation of methyl 4-nitrobutyrate proceeds to a 58.5% yield from nitromethane and methyl acrylate using benzyltrimethylammonium hydroxide as the basic catalyst. This is a pot reaction.
4. 2,2-Dinitropropane can be prepared in low yields from propane and nitric acid at high pressures. 2-Nitropropane is formed concurrently. Approximately 1-1.5 lb. of propane and 4-5 lb. of nitric acid (100% basis) were consumed per pound of dinitropropane.
5. When cyclohexene was nitrated with nitric acid under high pressure, cyclohexene nitrosite, nitrocyclohexenes, and a mixture of oils were produced.
6. In the high pressure system, nitric acid and cyclohexanone yielded only adipic acid at all working temperatures.
7. 2-Nitrobutane can be converted to 2,2-dinitrobutane by nitric acid under 2000 psi pressure. The yields are low.
8. No product was found when 1-nitropropane was reacted with nitric acid under high pressure.
9. By means of the Shechter-Kaplan reaction, 1-nitropropane was converted to 1,1-dinitropropane; 1-nitrobutane was converted to

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1,1-dinitrobutane; and 2-nitrobutane was converted to 2,2-dinitrobutane in yields of 80% or better.

10. By means of the Shechter-Kaplan reaction, 2000 lb. of 2,2-dinitropropane were prepared from 2-nitropropane in the pilot plant in 0.176 lb. mole runs. Yields averaged 89.7% and silver nitrate recoveries averaged 98.1%.

11. 4,4-Dinitroheptanedioic acid has been produced in the pilot plant from nitromethane and methyl acrylate. The Shechter-Kaplan reaction was used. The overall yield to the acid was 36%.

12. The process for the preparation of 2,2-dinitro-1,3-propanediol has been examined and a choice of solvents made. Isopropyl acetate is recommended as a solvent to extract the product from the aqueous solution, and ethylene dichloride is recommended as a recrystallization solvent. Yields of 50% are obtained.

13. The preparation of dinitropropanol has been investigated and the Shechter-Kaplan reaction favored over the Ter Meer reaction. Yields of dinitropropanol up to 80% have been obtained in the lab from nitroethane and formaldehyde; however, the product is difficult to obtain pure, and a yield of 65% can be expected in the pilot plant.

14. The esterification of dinitropropanol to produce dinitropropyl acrylate is difficult. Our study favored the process using acrylyl chloride and aluminum chloride over the catalytic esterification or transesterification. The reaction is fast, uses low temperatures and produced a monomer in 75-80% yield that can be polymerized without distillation.

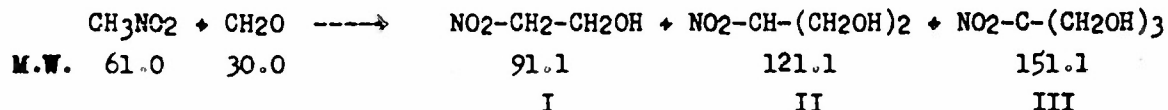
15. The polymerization of dinitropropyl acrylate to a high molecular weight polymer is best achieved using methyl amyl ketone peroxide as a catalyst in 0.25% in block or mass type procedure. The temperature is kept low, 40-50°C., and the time required is 50-60 hrs.

16. Cost estimates have been made for the pilot plant work on the reported processes where the reaction size is 0.15 lb.-mole to 0.50 lb.-mole. Labor is the major item in most compounds but is an item that can be reduced on scaling to larger reaction sizes. These estimates are based on laboratory work and work which has been performed in the pilot plant itself.

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II. TECHNICAL DEVELOPMENTSA. PREPARATION OF NITROETHANOL BY COLUMN REACTOR1. Discussion

The preparation of nitroethanol has been studied by Aerojet-General on a batch-wise and continuous method (1). The reported yields are 31 to 50%.

Equation 1

As the by-products II and III in this reaction need additional formaldehyde, one means of decreasing their production is a large excess of nitromethane. This has been achieved by using a column as the reactor with the nitromethane being continually refluxed (2). As the nitroethanol is formed it descends the column and the catalyst is neutralized. Using a 2 in. by 4 ft. column packed with stainless steel saddles, average yields of 66% of nitroethanol were obtained.

The reaction was also studied at 200 mm. of mercury pressure, where yields were 20-30% as compared to 66% at atmospheric pressure. A column shorter than 4 ft. gave a lower yield. More compact packing lowered the amount of nitromethane refluxed, thus lowering the yield.

2. Experimental

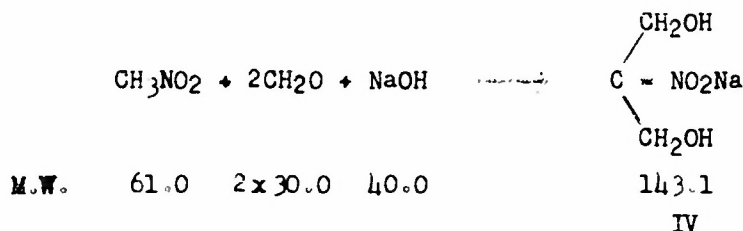
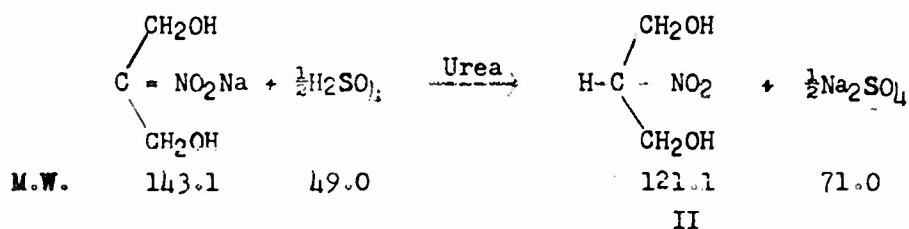
A 2 in. by 4 ft. heated column, packed with stainless steel saddles was fitted at the top with a reflux condenser through which a dropping funnel introduced the basic formaldehyde solution. Ten moles (610 g.) of nitromethane with 150 ml. of water and 20 ml. of 1 normal hydrochloric acid were placed in the still pot and refluxed strongly. The 4 moles (300 ml.) of 37% formaldehyde solution, made basic with 5.5 ml. of 10% sodium carbonate, were added so that the mole ratio of nitromethane to formaldehyde was 75-85 to 1 in the reaction zone.

After the addition was complete the reaction mixture was evaporated at 50 mm. until the liquid temperature rose to 65°C. The residue was azeotropically distilled with phenyl ether at reduced pressure. After extracting the nitroethanol layer with n-hexane to remove dissolved phenyl ether, there were obtained 240 g. (2.64 moles, 66%) of 2-nitroethanol. Five moles of nitromethane were recovered.

B. PREPARATION OF 2-NITRO-1,3-PROPANEDIOL (NPD)1. Discussion

2-Nitro-1,3-propanediol was a compound of some interest so the processes of preparation were examined. The compound can most directly be prepared from nitromethane and formaldehyde in a mole ratio of 1:2 and condensed under basic conditions. The reaction is an equilibrium one in which nitroethanol and tris(hydroxymethyl)nitromethane are also formed. Gorsky (3) states that the maximum yield of NPD is when the starting mole ratios of nitromethane to formaldehyde are 5:1. This value is in agreement with our data. Purification is the most difficult problem in this method. Nitroethanol can be stripped off by the use of a falling film evaporator, the residue from which yields a technical grade of NPD. The crude material can be recrystallized from several solvents, butanol seems to be desired, but recoveries are not too good. This method of preparation is hazardous and the product still contains some tris(hydroxymethyl)nitromethane.

The NPD can be prepared free of nitroethanol and tris(hydroxymethyl)nitromethane by first forming the sodium salt of NPD, followed by acidification and extraction.

Step 1Step 2

Various acids have been used in step 2 but the presence of urea or hydroxylamine seems to be beneficial (4). Dilute sulfuric acid (15%) in the presence of urea proves to be the most economical reagent. The sodium NPD was acidified by passing a water solution through an acid resin column. The ether extract of the resulting solution gave a poor quality material in 20% yield.

Attempts were made to free the NPD from the sodium salt or the calcium salt in nonaqueous media. No satisfactory results were obtained.

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The NPD can be continuously extracted from the aqueous solution with ethyl ether to give a product of good quality, but 24 hr. are required for this operation. The NPD can be extracted with ethyl acetate in a four-step batch extraction, the product from which is acceptable but not as good in color or melting point as from the ether extraction.

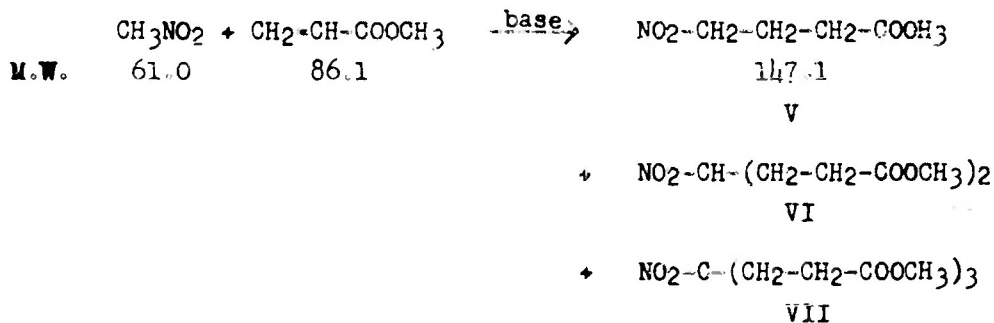
As a means of finding the optimum solvent for the extraction step, the distribution coefficients of NPD between several solvents and water were determined. The solvents investigated were ethyl ether, butyl acetate, nitromethane, ethyl acetate, 1-butanol at 25°C., and 1-butanol at 50°C. The coefficients expressed as $\frac{\text{concentration in solvent layer}}{\text{concentration in water layer}}$ for a 0.55 molar solution were 0.058, 0.16, 0.20, 0.41, 0.66, and 0.74, respectively. Thus butanol seems to be the solvent of choice. Furthermore, the evaporation of the butanol solution removes dissolved water as the azeotrope. The dry product can be recrystallized from butanol or ethyl ether. The best quality of product is obtained when ethyl ether is used as the recrystallization solvent.

The butanol extract can be concentrated and reduced with hydrogen over Raney nickel catalyst. A 21% yield of 2-amino-1,3-propanediol was obtained based on the starting nitromethane.

2. Experimental

To a stirred mixture of 122 g. (2.0 moles) of nitromethane, 300 ml. (4.0 moles) of 37% formaldehyde solution, 100 ml. of water, and 250 ml. of methanol in a flask surrounded by an ice bath was added dropwise 90 g. (2.0 moles) of sodium hydroxide in solution in 180 ml. of water. The salt precipitated. The slurry was stirred for 2 hr. and filtered at 0°C. The filter cake was returned to the reaction flask and ice bath, made a slurry with 100 ml. of water and 25 g. of urea added. The pH was slowly brought to 3.5-4.0 with 15% sulfuric acid. The solution was filtered to remove precipitated sodium sulfate and was then extracted four times with butanol. The solution was evaporated under reduced pressure. The remaining oil was chilled and seeded to obtain 81.0 g. (0.67 mole, 33.5%) of light colored, solid NPD, m.p. 50-52°C. A second crop was obtained, 31.5 g. (0.25 mole, 13%), that was darker in color, m.p. 42-46°C. The total yield of two crops was 46.5%.

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C. PREPARATION OF METHYL 4-NITROBUTYRATE1. Discussion

The preparation of methyl 4-nitrobutyrate from nitromethane and methyl acrylate is a reaction which is slow, gives poor yields, and produces several side reactions. As in the case of nitroethanol the amounts of by-products formed can be decreased by a single mass action effect, large excesses of nitromethane. A column type reactor similar to that used for the nitroethanol study was tried but due to solubilities, and reaction rates, no condition was found that produced product.

When the column reactor failed, the pot reaction was examined briefly. Kloetzel (5) found triethylamine one of the best catalysts for this type of reaction. With triethylamine at room temperature, we obtained 15% yield of product after 2 days, 34% after 4 days, and 42% after 9 days. When methyl isopropylamine was used as the catalyst and the reaction refluxed for 1 hr., 43.5% of product was obtained. When benzyltrimethylammonium hydroxide was the catalyst and the reaction was refluxed for 2 hr., the yield was increased to 58%.

2. Experimental

One mole (86 g.) of stabilized methyl acrylate, 610 g. (10 mole) of washed nitromethane, and 10 ml. of 40% benzyltrimethylammonium hydroxide in water solution were refluxed together for 2 hr. The reaction mixture was washed with 100 ml. of water containing 5 ml. of 6 normal hydrochloric acid. After evaporating the nitromethane solution at reduced pressure, the residue was distilled to obtain 86.0 g. (0.585 mole, 58.5%) of methyl 4-nitrobutyrate at 85°-100°C. (1-2 mm.).

D. LIQUID PHASE NITRATION OF PROPANE1. Summary

Potentially, the lowest manufacturing cost for 2,2-dinitropropane (DNP) can be achieved by the direct nitration of propane. Previous work indicated that heat transfer and temperature control were major difficulties in operation of a continuous reactor. A reactor was built, using circulating hot water under pressure as the temperature control medium. Due to early mechanical failures, no appreciable quantity of DNP was produced by direct nitration before the 2000 lb. order was produced by indirect nitration of 2-nitropropane (2NP), thus this work was limited to obtaining data and not for pilot plant production.

Most of the data reported are based on runs made with only propane and nitric acid in the feed. For these runs, it appears that the optimum mole ratio of feed reactants is about 2:1, $\text{HNO}_3:\text{C}_3\text{H}_8$. Considerable 2NP production results when no 2NP is added to the feed. At a 2:1 mole ratio of $\text{HNO}_3:\text{C}_3\text{H}_8$, conversions of HNO_3 were about 5% to DNP and 4.6% to 2NP, and conversions of propane about 3.5% to DNP and 9.5% to 2NP. Material balances were not obtainable with any of these runs and yields could not be calculated.

Three runs were completed with 2NP added to the feed mixture. Complete material balances were made on two of these runs and yields calculated. Yields for the best run were:

Propane to DNP	--	26.4%
Propane to 2NP	--	33.6%
HNO_3 to DNP	--	14.5%
HNO_3 to 2NP	--	9.3%

2. Apparatus

The reactor consisted of two sections of $\frac{1}{2}$ in., schedule 80 stainless steel pipe (316), each about 20 ft. long. Each section was jacketed with $1\frac{1}{2}$ in. insulated pipe to contain the circulating water. Each section was fitted with a thermowell, about 18 ft. long, made of $\frac{1}{4}$ in. O.D. high pressure stainless steel tubing. Two thermocouples were placed in each thermowell in addition to a thermocouple placed on the outside of the reactor at the bend between the two reactor sections. A third section, similar to the reactor sections, was used as a cooler with cold water passed through the annular space. A "Minim" pressure control valve was placed after the cooler section to maintain the desired reactor pressure.

The circulating water was returned to a 300 psi "boiler", containing about 25 gal. of water. The unit was heated with 18 1500-watt heaters (230 volts) and the temperature was controlled by a Partlow controller operating a solenoid switch. The hot water was circulated by a Dean Bros. centrifugal pump with "Synseal" hydraulic packing.

The high pressure pumps used to feed reactants were Milton-Roy basic design, modified with Hills-McCanna ball check valves. Nitric acid

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was pumped from a weigh tank with one pump and propane with another. The two reactants were pumped through separate lines and were combined at a tee just ahead of the reactor. When 2NP was part of the feed, it was dissolved in the acid.

The crude reactor product, after passing through the pressure controller, entered a liquid-gas separator where the gaseous products were vented. The liquid product usually consisted of oil and acid layers and these were steam stripped to remove the contained oil. The 2NP was then separated from the DNP by fractionation.

3. Experimental Data

Table I is a compilation of the basic data and results of runs which yielded enough information to permit evaluation. Tables II and III are data needed to evaluate the runs.

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Table I

EXPERIMENTAL I

Pressure - 1000 psi (except

Run No.	Av. Reactor Temps		Mol. Ratio		Conversions - Mol. %				
	°C.		Feed		Propane to		HNO ₃ to		2NP to
	Low	High	HNO ₃ C ₃ H ₈	HNO ₃ 2NP	2NP	DNP	2NP	DNP	DNP
383850R	203	210	0.39		2.2(1)	0.5	5.6(1)	2.5	-
64	206	221	0.70		1.6(1)	0.8	2.2(1)	2.3	-
66	211	226	0.86		2.1(1)	1.1	2.4(1)	2.6	-
61	212	223	0.99		5.9(1)	1.9	5.9(1)	3.8	-
74	202	222	1.07		10.1	2.6	9.4	4.9	-
71	198	218	1.13		8.5	2.4	7.6	4.2	-
56	210	220	1.89		8.4(1)	4.9	4.4(1)	5.2	-
77	195	210	2.01		9.1	3.5	4.5	3.4	-
79	208	220	2.03		9.6	5.0	4.7	4.9	-
78	194	209	2.38		9.1	3.3	3.8	2.8	-
75	199	207	3.28		9.5	7.6	2.9	4.6	-
76	193	200	3.78		11.6	5.7	3.1	3.0	-
70	212	216	3.86		8.6	6.6	2.2	3.4	-
80	197	211	2.05	10.9	2.3	8.3	1.1	8.1	-
81	199	220	1.84	5.5	-	5.1	-	7.4	10.1
82	197	231	1.82	5.5	9.1	8.3	5.0	9.1	-

(1) 2NP recovery probably
high temp. (ca 100°C.)RECALCULATE I

	Mol. Ratio					#L ³ Requirement ³
	Feed	#C ₃ H ₈	#Gas	#Oil	#HNO ₃	
	HNO ₃ C ₃ H ₈	Hr. (Calc.)	Hr.	Hr.	F ³ HNO ₃ (100%) #DNP	
363881R	2.44	2.64	9.3	3.15	0.	3.46
363882R	3.62	1.75	7.4	4.06	0.	6.45

1 All 2NP changed assumed

2 2NP produced per lb. DN

3 Calculated by assuming
HNO₃ in acid layer; 2NF

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Table I

EXPERIMENTAL DATA

Pressure - 1000 psi (except 363882R = 2000 psi)

Run No.	Av. Reactor Temps		Mol. Ratio Feed HNO ₃ C ₃ H ₈ 2NP	Acid Strength Wt % HNO ₃	- Feed Rate -		Space Velocity Vol. Feed/Hr. Vol. Reactor	Product					Conversions - Mol. %					
	Low	High			#Acid Hr.	#C ₃ H ₈ Hr.		#2NP Hr.	Loss #Gas Hr.	#Oil Hr.	Wt. % DNP in Oil	#DNP Hr.	#2NP Produced Hr.	Propane to 2NP	HNO ₃ to 2NP	DNP	2NP to DNP	
383850R	203	210	0.39	60.5	12.0	13.0	27	9.0	16.0	0.76	25.0	0.19	0.57	2.2(1)	0.5	5.6(1)	2.5	-
64	206	221	0.70	60.5	20.3	12.3	27	14.1	18.5	0.69	43.0	0.30	0.39	1.6(1)	0.8	2.2(1)	2.3	-
66	211	226	0.86	60.5	20.8	10.2	24	14.0	16.0	0.78	45.3	0.35	0.43	2.1(1)	1.1	2.4(1)	2.6	-
61	212	223	0.99	60.5	19.0	8.0	19	14.7	12.3	1.41	32.7	0.46	0.95	5.9(1)	1.9	5.9(1)	3.8	-
74	202	222	1.07	59.2	15.6	6.0	15	13.2	8.4	1.70	28.1	0.48	1.22	10.1	2.6	9.4	4.9	-
71	198	218	1.13	59.2	16.3	6.0	15	13.7	3.6	1.16	29.6	0.43	1.03	8.5	2.4	7.6	4.2	-
56	210	220	1.89	60.5	19.3	4.3	13	15.2	8.4	1.38	47.4	0.65	0.73	8.4(1)	4.9	4.4(1)	5.2	-
77	195	210	2.01	61.1	16.5	3.5	10	13.8	6.3	1.01	36.6	0.37	0.64	9.1	3.5	4.5	3.4	-
79	208	220	2.03	58.1	18.8	3.8	11	15.8	6.8	1.30	43.9	0.57	0.73	9.6	5.0	4.7	4.9	-
78	194	209	2.38	61.1	19.5	3.5	11	17.1	5.9	0.99	35.4	0.35	0.64	9.1	3.3	3.8	2.8	-
75	199	207	3.28	61.1	18.0	2.3	9	16.1	4.2	0.99	54.0	0.54	0.45	9.5	7.6	2.9	4.6	-
76	193	200	3.78	61.1	17.8	2.0	8	15.8	4.0	0.82	42.2	0.35	0.47	11.6	5.7	3.1	3.0	-
70	212	216	3.86	59.2	20.5	2.2	9	18.1	4.6	0.82	53.6	0.44	0.38	8.6	6.6	2.2	3.4	-
80	197	211	2.05	58.1	15.1	3.0	10	11.3	8.1	2.02	37.4	0.75	+0.14	2.3	8.3	1.1	8.1	-
81	199	220	1.84	58.1	15.9	3.5	11	11.6	10.2	3.04	29.8	0.91	-0.25	-	5.1	-	7.4	10.1
82	197	231	1.82	58.1	15.7	3.5	7	12.4	9.1	3.86	22.8	0.88	+0.64	9.1	8.3	5.0	9.1	-

(1) 2NP recovery probably low, due to operation of cooler at too high temp. (ca 100°C.)

RECALCULATED BY MATERIAL BALANCE

Run No.	Mol. Ratio Feed HNO ₃ C ₃ H ₈		#C ₃ H ₈ Hr.	#Gas Hr.	#Oil Hr.	#DNP ³ Hr.	#2NP ³ Produced Hr.	Conversions			Yields ³			Net Raw Material Requirement ³		
								Propane to			HNO ₃			2NP to		
								2NP	DNP	2NP	2NP	DNP	DNP	DNP	DNP	DNP
363881R	2.44	2.64	9.3	3.15	0.94	-0.17	-	8.5	-	8.3	7.2	100 ¹	-	1.35	0.18	3.46
363882R	3.62	1.75	7.4	4.06	0.93	+0.78	22.1	17.3	6.1	9.5	-	-	-	1.24	-0.84	6.45

1 All 2NP charged assumed converted to 2,2-DNP.

2 2NP produced per lb. DNP produced.

3 Calculated by assuming complete recovery of unreacted C₃H₈, NO, HNO₃ in acid layer, 2NP and DNP.

Table IIGAS ANALYSES - DRY BASIS

	<u>Time</u>	<u>Mole %</u>		(AR96765 & AR96779)						
<u>363875</u>		CO	CO ₂	N ₂ O	NO ₂	NO	N ₂	C ₃ H ₈	Argon	
	3:00 p.m.	6.7	21.2	1.9	0.11	45.1	5.0	20.1	0.01	
	3:30 p.m.	9.0	18.2	1.5	0.10	37.2	0.0	34.0	0.00	
76										
77										
78	Samples contained with air									
79										
80										
363881	5:30 p.m.	6.6	21.5	4.8	0.1	41.4	6.8	18.7	0.0	
"	6:00 p.m.	6.2	21.6	5.0	0.2	40.0	7.1	19.9	0.0	
363882	8:15 p.m.	10.0	30.2	10.5	0.3	19.0	23.2	6.8	0.0	
"	8:30 p.m.	11.1	29.7	9.9	0.3	21.0	20.8	7.4	0.0	

Table IIIANALYSES OF ACID LAYER (CRUDE PRODUCT)

		<u>Wt %</u>		<u>Solids</u>		<u>Fe</u>		<u>PPM</u>		<u>Corrosion Rate</u>	
		<u>AR</u>	<u>HNO₃</u>	<u>Wt. %</u>				<u>Ni</u>	<u>Cr</u>	<u>Calculated Metals loss,</u>	
										<u>lb/lb DNP + 2NP produced</u>	
363861	96609	16.9	0.28	600	300	670				0.015	
64	96610	17.8	-	1180	250	821				0.044	
66	96611	16.0	-	700	340	805				0.032	
81	96663	20.6	0.36	602	228	238				0.014	
82	96663	18.4	0.20	150	20	166				0.0019	

4. Conclusions

The prime variable studied in this work was the effect of mole ratio of reactants on the product distribution and conversion. Attempts were made to make complete material balances and subsequent yield calculations, but this was possible in only two cases and these yield figures are of doubtful accuracy.

The temperature range was maintained relatively constant, 200 to 230°C., maximum. This was based on past experience and the fact that this was about the pressure limitation of the hot water cooling system. Some runs were attempted at higher temperatures, but invariably run-away temperatures resulted when operation above about 235°C. was attempted.

Space velocity received only incidental study, since the range of pump capacities was limited over the range of mole ratios used. Total feed rates varied from 19 to 32 lb. per hour.

No attempt was made to study the effect of nitric acid concentration. All runs were made with approximately 60% HNO_3 , but it was observed that better temperature control was possible when using 58% HNO_3 than with 61% HNO_3 . There seemed to be a critical concentration at which excessive oxidation would occur, but this point was investigated only qualitatively.

Figure 5 is a graphic representation of the effect of mole ratio of $\text{HNO}_3/\text{C}_3\text{H}_8$ on conversion. It will be noted that the questionable data for conversion to 2NP at ratios below 1.0 are not shown, and there are indications that the conversions to DNP at the lower mole ratios are also in error on the low side.

The optimum mole ratio is difficult to determine, but it appears to lie between 1/1 and 2/1, $\text{HNO}_3/\text{C}_3\text{H}_8$. These figures are for a feed containing no 2NP. Comparing the results of runs 80 and 81, it appears that a feed ratio of $\text{HNO}_3:\text{C}_3\text{H}_8:2\text{NP}$ of about 8:4:1 at 1000 psi might result in the formation of no net 2NP.

The effect of pressure was checked in only two runs, 81 and 82. Considerable net production of 2NP was noted at 2000 psi (although it should be remembered that run 82 was operated at a slightly higher temperature), with no loss in DNP production. This point should be evaluated more fully, and it can be speculated that the ratio of feed might conveniently be as high as 16:8:1, $\text{HNO}_3:\text{C}_3\text{H}_8:2\text{NP}$, at the higher pressure.

The data of Table III also indicate that operation at 2000 psi may decrease the corrosion rate by several fold. Taking the corrosion rate data and DNP production rates for runs 81 and 82, it can be estimated that the life of the present reactor (15% loss of metal) at 1000 psi would be about 23 days with a production of about 530 lb. of DNP, while a pressure of 2000 psi would permit a production of 3900 lb. of DNP in about 177 days before reactor replacement. The investigation of pressure to decrease corrosion rate may reveal that higher pressure operation may obviate the need for a tantalum-lined reactor.

At the beginning of work, a running plot was kept of the effect of mole ratio on conversions, and it appeared that considerable progress was being made in determination of optimum conditions. It was not realized until the work was completed that the yield figures were so low. It is difficult to even speculate what conditions could be changed to effect an improvement in the yield figures. Several additional runs are needed with complete data necessary for material balances, first to confirm or disprove the data of runs 80-82 and to supply data for several intermediate conditions.

E. MISCELLANEOUS NITRATION STUDIES IN THE LIQUID PHASE**1. Nitration of Cyclohexene**

In an attempt to obtain some nitro or polynitro compounds, the liquid phase nitration of cyclohexene was undertaken. Cyclohexene was reacted with 10, 20, 30, and 67% nitric acid at 1000 lb. per square inch pressure, and temperatures from 30 to 130°C. Also, cyclohexene was reacted with 20% nitric acid in acetic anhydride at 1000 psi and 60°C. The mole ratio of nitric acid to cyclohexene was 4-1, and the contact time in the heated zone was 20 min. With 10% acid below 100°C. there was no reaction and above 30°C. with 67% acid complete oxidation predominated. In all intermediate cases oil was formed, solid in some.

At 70°C., 30% nitric acid, conditions were best for the formation of solids, being 8% by weight of the reacted cyclohexene. Oil was formed in 33% by weight at the same time. With 20% nitric acid in acetic anhydride at 60°C., 48 g. of oil were obtained from 47 g. of cyclohexene fed.

In a series of studies of dinitrogen tetroxide and olefins, Baldock, Levy, and Scaife (6) made a rather complete study of the reaction products when dinitrogen tetroxide and cyclohexene were reacted with and without solvent. A solid was formed in 3% yield which had been known by Baeyer (7) as the cyclohexene nitrosite (m.p. 150°); by Wieland and Blumlick (8) as the nitrosite (m.p. 145°); and by Bloomfield and Jeffrey (9) as the cyclohexene pseudo-nitrosite (m.p. 153°). Wieland suggested that the solid material was a dimer, and the work of Bloomfield and Jeffrey proves the point. Bloomfield, working with nitric oxide in solvents, obtained the pseudo-nitrosite, nitro-cyclohexenes, and unstable viscous oil. Baldock was able to separate the oil into 2-nitrocyclohexylnitrate, 1,2-dinitrocyclohexane, and 2-nitrocyclohexanol. The latter arising from the hydrolysis of 2-nitrocyclohexylnitrite.

The solid obtained from the liquid phase nitration of cyclohexene in our work has a decomposition point of 150-151°C. after recrystallization from glacial acetic acid. After recrystallization from ethyl acetate, the melting point was 149-150°C. (dec.).

Analysis required for nitronitrosohexane dimer, $(C_6H_{10}N_2O_3)_2$:
C, 45.6; H, 6.3; N, 17.6.

Found: C, 45.1; H, 6.3, N, 17.3.

A fractionation curve (Appendix B) of the oil obtained from cyclohexene and aqueous 20% nitric acid at 100°C. indicates a complex mixture. A cut at 35-45°C. at a pressure less than 1 mm. had the analysis: C, 55.0; H, 7.1; N, 10.7. Required for isomeric nitrocyclohexenes, $C_6H_9NO_2$: C, 56.7; H, 7.1; N, 11.0. A sample of the oil was oxidized with alkaline permanganate and a solid material obtained. After the solid was recrystallized from nitric acid, the melting point, 151-152°C. (recorded for adipic acid, 151-153°C.), and solubility indicate adipic acid. This confirms the suggestion that some of the light oil was 1-nitrocyclohexene.

One cut of the oil at 48-50° (less than 1 mm.) gave the analysis: C, 59.1; H, 7.8; N, 9.5, which corresponds to $C_6H_9.4N_{0.8}O_{2.6}$. Another cut at 100-101°C. (less than 1 mm.) analyzed: C, 48.0; H, 6.3; N, 10.2, corresponding to $C_6H_9.3N_{1.1}O_{3.3}$. Obviously these oils were not pure compounds.

2. Attempted Nitration of Cyclohexanone

In attempts to introduce the nitro group into a cyclic compound, or to break the cyclic chain and retain nitro groups, cyclohexanone was used as the example of the cyclic ketones. When cyclohexanone and 30% nitric acid were reacted for 20 min. at 1000 psig in the high pressure system, the only product isolated was adipic acid, m.p. 150-151°C. Seven temperatures were used, ranging from 80°C. to 180°C. At the higher temperatures, the yields were lower and more gas was formed.

<u>Temperature, °C.</u>	<u>Yield of Adipic Acid</u>
80	39
90	40
100	45
120	43
140	49
160	37
180	29

A run was made using 90% nitric acid in one stage of the pump and cyclohexanone dissolved in acetic anhydride in the other stage of the pump. Directly following the mixing point, at room temperature, excessive heating took place and after 40 min. of the run the line plugged from decomposition residue. No product could be isolated.

3. 2-Nitrobutane Nitration

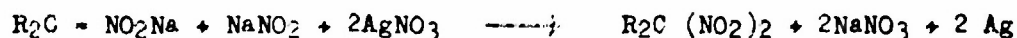
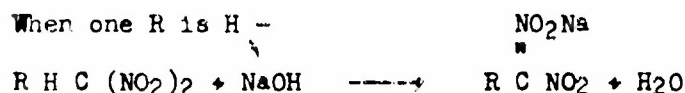
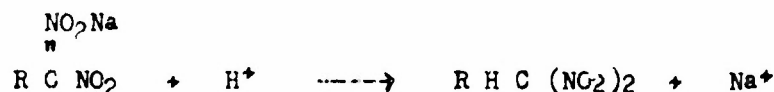
2-Nitrobutane was nitrated in the pressure system at 1000 psig and 180°C. with 62% nitric acid. When the nitric acid to nitrobutane mole ratio was 3 to 1, a 10% yield of 2,2-dinitrobutane was obtained. Of the original 2-nitrobutane, 36% was recovered.

4. Attempted Nitration of 1-Nitropropane

In an attempted pressure nitration of 1-nitropropane at 1000 psig and 180°C with 62% nitric acid there was excessive gassing. Of the 4550 ml. of total material fed to the reactor, only 2770 ml. were recovered as product. From this reaction product, the only compound obtained was 10% of the original 1-nitropropane.

F. PREPARATIONS BY THE SHECHTER-KAPLAN REACTION1. Discussion

As a means of becoming more familiar with the Shechter-Kaplan procedure for introducing the second nitro group of a gem dinitro group into a nitroparaffin, several compounds were made. The compounds were known, so very little development was undertaken other than to adapt the general isolation procedure most desirable for any specific compound. In general, the nitroparaffins containing gem dinitro groups removed from the end carbon can be conveniently steam distilled from the reaction mixture. Those compounds containing a 1,1-dinitro group gave trouble in steam distillation, mostly foaming of the silver precipitate, and were isolated by first forming the sodium salt with an equivalent of sodium hydroxide, filtering the silver from the solution, regenerating the nitroparaffin with acid, and collecting the oil that separated. The general reaction is:

Step 1Step 2Step 3Step 42. Experimental for 1,1-Dinitropropane

To 250 ml. of water, the following were dissolved in order: 22.5 g. (0.55 mole) of sodium hydroxide, 45 g. (0.50 mole) of 1-nitropropane, and 37.5 g. (0.55 mole) of sodium nitrite. This solution was then added rapidly with stirring to 170 g. (1.0 mole) of silver nitrate dissolved in 500 ml. of water with 150 g. of ice present so that the temperature did not exceed 25°C.

After stirring for one-half hour, 38 g. (0.5 mole) of 48% sodium hydroxide were added slowly. After filtration, the filtrate was cooled to 0° and acidified to a pH of 3 with 20% sulfuric acid, 35 g. of hydroxylammonium chloride being present. The oil that separated was removed, then combined with two ether extracts of the aqueous layer. The 58.6 g. (0.437 mole, 87%) of oil that remained after removal of the ether was steam distilled to obtain 53.5 g. (0.40 mole, 80%) of dry, undistilled 1,1-dinitropropane.

3. Experimental for 2,2-Dinitrobutane

Using 412 g. (4.0 moles) of 2-nitrobutane, 180 g. (4.4 moles) of sodium hydroxide and 300 g. (4.4 moles) of sodium nitrite in 1500 ml. of water, the reaction was carried out in the same manner as was the preparation of 1,1-dinitropropane. The addition to 8 moles of silver nitrate, pH about 6, was carried out in a 12-liter flask from which the product was later steam distilled to obtain 512 g. (3.46 mole, 86.6%) of dried 2,2-dinitrobutane.

4. Experimental for 1,1-Dinitrobutane

There were dissolved in 1500 ml. of water 180 g. (4.4 moles) of sodium hydroxide, 412 g. (4.0 moles) of 1-nitrobutane, and 300 g. (4.4 moles) of sodium nitrite, and the solution was cooled to tap water temperature. To 8.0 moles of recovered silver nitrate in $3\frac{1}{2}$ liters, pH about 6, was added with vigorous agitation 1 Kg. of ice followed by the prepared nitrobutane solution.

After stirring for one hour, 170 g. (4.0 moles) of sodium hydroxide as a 50% solution was added and stirring continued for one-half hour. After filtration, the filtrate was acidified at 10°C. with 20% sulfuric acid. The oil was separated and dried to yield 471 g. (3.18 moles, 79.6%) of 1,1-dinitrobutane.

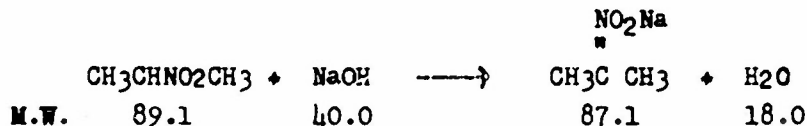
5. Attempted Preparation of 1,1-Dinitro-2-butanol

In attempts to prepare 1,1-dinitro-2-butanol from 1-nitro-2-butanol by oxidative-nitration, no product was obtained. When the starting materials, nitromethane and propanal, were used, only nitrobutanol could be isolated.

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Page 16G. PILOT PLANT PRODUCTION OF 2,2-DINITROPROPANE1. Discussion

By the use of the nitration reaction of Shechter and Kaplan, 2000 lbs. of 2,2-dinitropropane (DNP) were made from 2-nitropropane in small batches in the pilot plant. The reaction is:

Step 1Step 2

Benefits to be gained from the production were knowledge of the general procedure in the pilot plant, and a basis on which to compare the production by this method to the high pressure nitration procedure. The runs were made with nontechnical operators on a three-shift basis; therefore, supervision was not continuous. In an operation of this size the labor dominates the production cost, however, the silver nitrate recovery is of greatest importance for scale-up calculations. Of the 99 batches made, 88 batches in which no mechanical difficulties were encountered have been studied for variables:

Silver Nitrate Recovery

Mean recovery ($\bar{X}$) (by analysis of subsequent solution): 98.1%

Mean deviation $\frac{\sum(X-\bar{X})}{n}$: 1.4

Variance $\frac{\sum(X-\bar{X})^2}{n-1}$: σ^2 = 2.9

Standard deviation or standard error: σ = 1.7

Less than 0.06 pounds per run (0.1%) of the silver nitrate appeared in the filtrate of the reaction.

Product

Mean yield of DNP: 21.1 lbs. or 89.7%
Mean melting point of DNP: 48.4°C.

2. Experimental

The wet silver cake from the previous run which averages 67 $\pm$ 4 lbs. is placed in a stainless steel vessel and concentrated nitric acid equivalent to 29.7 lbs. (0.472 lb.-mole) of pure acid is added in portions. After the reaction has subsided, 40 lbs. of water are added and the solution is agitated and heated in a water bath to 90°C. When the silver is all dissolved, cool, bring to 200 lbs. of total solution and analyze for silver nitrate; average analysis is 58.8 lbs. From the analysis add silver nitrate to bring the total weight of silver nitrate in solution to 60.0 lbs. (0.352 lb.-mole) and adjust the pH at 5.5 to 6.0 with sodium hydroxide.

To this silver nitrate solution at 15 to 20°C. is added as rapidly as possible and with vigorous agitation the following solution: 220 lbs. of water, 7.7 lbs. (0.183 lb.-mole) of 95% flake caustic, 16.0 lbs. (0.179 lb.-mole) of 2-nitropropane, and 13.2 lbs. (0.183 lb.-mole) of 95% sodium nitrite. By the use of cooling water the reaction kettle is held to 25°C.

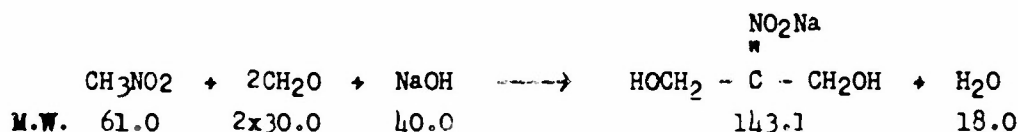
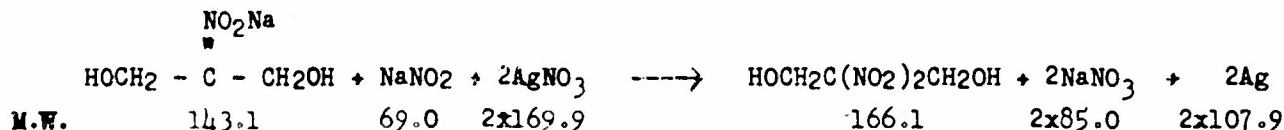
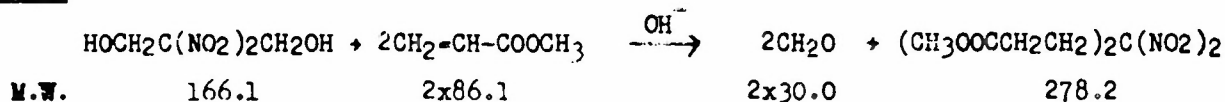
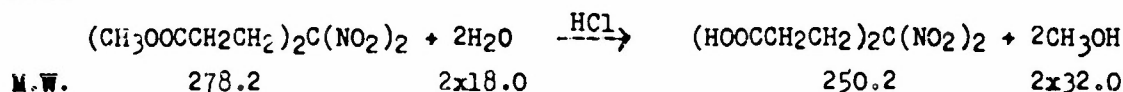
After stirring the reaction for $\frac{1}{2}$ hr., the slurry is pumped to a kettle where it is steam distilled to obtain 21.1 $\pm$ 1.0 lbs. (0.158 lb.-mole; 89.7 $\pm$ 4.7%) of 2,2-dinitropropane. The steam distillate water is used as make-up for subsequent reaction batches. The material remaining in the kettle is filtered and the silver cake reconverted to silver nitrate. The filtrate is analyzed for silver and if negative, discarded. The freezing point of the solid product is 48.4°C. with a mean deviation of 1.0°C.

The time per batch averaged 11 hrs. Two batches were run concurrently, so that the silver nitrate recovery was handled for one batch as the other batch was being run.

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Page 18H. PREPARATION OF 4,4-DINITROHEPTANEDIOIC ACID1. Discussion

The method of Aerojet (10) was used to prepare methyl 4,4-dinitroheptanedioate on a 0.15 lb.-mole scale in the pilot plant. The yield from nitromethane was 39% as compared to the reported 36.5%. The ester was hydrolyzed to 4,4-dinitroheptanedioic acid in 18% hydrochloric acid in 92.5% yield. The reactions are:

Step 1Step 2Step 3Step 42. Experimental

A slurry of sodium 2-nitro-1,3-propanediol is prepared by adding 6.9 lb. (0.16 mole) sodium hydroxide in 15 lb. water to a solution of 9.2 lb. (0.15 mole) nitromethane, 24.3 lb. (0.30 mole) 37% formaldehyde solution, 15 lb. water and 15 lb. ice. The reaction vessel should be cooled externally as well as the ice used and should be well stirred. The sodium hydroxide is added so as to keep the temperature below 30°C., and the slurry that forms when about half the base has been added is stirred an additional hour. To the slurry is then added a solution of 11.5 lbs. (0.15 mole) sodium nitrite in 27 lb. of water, and stirring continued 15 min. When the temperature of the salt slurry is down to 15°C., it is ready for the nitration reaction.

A vat equipped with efficient stirring and cooling is charged with 51.0 lb. (0.30 mole) of silver nitrate or equivalent recovered silver nitrate solution. The pH of the solution is adjusted to 6.0±0.2 and the weight

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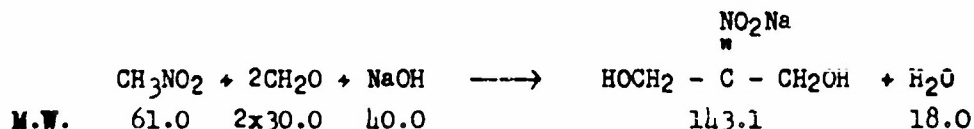
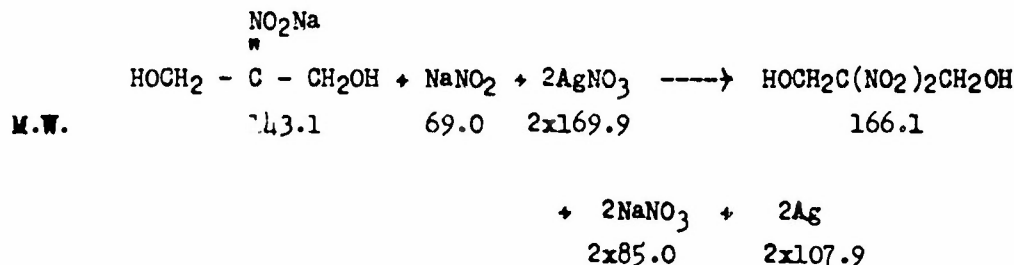
of the solution brought to 135 lb. To the silver nitrate solution is then added as rapidly as possible the sodium nitropropanediol slurry and the temperature is held under 30°C. A precipitate of flocculent green-gray silver is formed and after $\frac{1}{2}$ hr. stirring, the dinitropropanediol produced is deformedylated with 5.7 lb. of sodium hydroxide dissolved in 10 lb. of water. The pH is adjusted to 8.0. The reaction mixture is then filtered to remove the silver for subsequent recovery.

The filtrate from the reaction is warmed to 45°C. and 33 lb. (an excess) of methyl acrylate is added. The addition must be adjusted, to keep the temperature from rising too high and vaporizing the acrylate, and will require about 6 hrs. After stirring for 16 hrs., the solution has returned to room temperature and is filtered. A second crop is obtained which amounts to about one-fourth of the yield if the filtrate is allowed to stand several days and is cooled and filtered again. The total yield is 16.25 lb. (0.0585 mole; 39%) of dry, tan colored, methyl 4,4-dinitroheptanedioate, m.p. 42-44°C. The ester can be recrystallized from methanol in 95% recoveries.

The crude ester is placed in 45 lb. of 18% hydrochloric acid and refluxed for 12 hrs., after which the solution is concentrated to one-half its volume and cooled. There is obtained 13.5 lb. (0.054 mole; 36%) of white crystalline 4,4-dinitroheptanedioic acid, m.p. 138-140°C.

I. PREPARATION OF 2,2-DINITRO-1,3-PROPANEDIOL (DNPD)1. Discussion

We have examined the process for the preparation of DNPD from nitromethane and formaldehyde using the Shechter-Kaplan reaction. The reaction itself proceeded smoothly but the isolation of the product from the resulting aqueous solution was not desirable. A process that had been used that gave good quality product was to extract the solution with ethyl ether, then recrystallize the product from 1-chloro-1-nitroethane. The use of ether in the pilot plant is extremely hazardous. Ethyl acetate can be used as the extracting solvent but the quality of the resulting DNPD is poor. After considering the solvents available, both as to cost and usability, it was determined that isopropyl acetate as the extractant and ethylene dichloride as the recrystallizing solvent were preferred. The reactions are:

Step 1Step 22. Experimentala. Silver Nitrate Recovery

The silver cake filtered from previous runs, equivalent to 0.3 mole, is placed in a stainless steel or ceramic vessel which can be heated and agitated. The 27 lbs. (0.43 mole) of nitric acid, calculated to weight from the carboy analysis, is added in portions in a well ventilated hood. When the reaction has subsided, the solution is heated to the boiling point with agitation, and this is continued until all the metal has dissolved. The solution is made up to 150 lbs. total weight with chlorine-free water and the pH is adjusted to 5.9 with sodium hydroxide. A 100-g. sample is taken, diluted to one liter and aliquots titrated with standard ammonium thiocyanate solution using a ferric sulfate indicator. The amount of silver nitrate present in the solution is calculated and if not 51.0 lbs. (0.30 mole), it is

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made up to that weight by adding silver nitrate crystals. This solution is then ready for the reaction when cooled to 15°C.

b. Salt Preparation

A vessel with efficient cooling is required for this step. When unavailable, part of the water added must be replaced by crushed ice. Add to the vessel 9.2 lbs. (0.15 mole) of nitromethane, 9.0 lbs. (0.30 mole) of formaldehyde as 24.3 lbs. of 37% solution, and 47 lbs. of water. Agitate and chill the solution and slowly add 6.6 lbs. (0.16 mole) of tech. sodium hydroxide dissolved in 13 lbs. of water, keeping the temperature below 30°C. Cool before using to 15°C.

c. Shechter-Kaplan Reaction

The silver nitrate solution is placed in a vessel equipped with cooling coils or jacket and an efficient stirrer. The salt solution is added as rapidly as possible, holding the temperature below 25°C., and the resulting slurry is stirred for $\frac{1}{2}$ hr. The precipitated silver should be spongy in nature and green in color for easy filtering.

d. Product Isolation

The reaction mixture is filtered and the silver cake washed and returned for silver nitrate recovery. The filtrate is extracted by means of a packed column or batchwise by three extractions of isopropyl acetate, each volume of solvent being equal to one-half the volume of the extracted solution. The raffinate is discarded if no silver ions are present. If silver is present, it may be recovered by making the raffinate basic with hydroxide and filtering. The filtrate is now discarded and the precipitate of silver oxide is added to the silver cake for recovery.

No drying of the isopropyl acetate extract is necessary as the water-isopropyl acetate azeotrope will remove the dissolved water when concentrating. The extract is concentrated to the minimum volume, trying to remove all the acetate and keeping the liquid temperature below 45°C. The residue is then dissolved in 25 lbs. of ethylene dichloride at 80-82°C., filtered and treated with char if necessary and cooled to 5°C. After filtering off the crystallized DNPD, there should be 12 to 15 lbs. of dried DNPD. A second crop is obtained by evaporating and cooling the combined mother liquors.

J. PREPARATION OF 2,2-DINITROPROPANOL (DPL)1. Discussion

The problem of comparing the preparation of 2,2-dinitropropanol from 1-chloro-1-nitroethane by the Ter Meer (11) reaction and from nitroethane by the Shechter-Kaplan reaction was undertaken. The various paths of procedure and the yields are as shown on Fig. 1. The problem of preparing DPL in a grade pure enough so that crosslinking in the polymerization of the acrylate prepared from it is at a minimum hinges somewhat on the purity of the starting nitro compound. If the chloronitroethane is prepared from commercial nitroethane, Table IV illustrates the potential impurities.

TABLE IVBoiling Points at Atmospheric Pressure

2-Nitropropane	120.3°C.
Chloronitromethane	123°
1-Nitro-1,1-dichloroethane	124°
1-Nitro-1-chloroethane	125°
2-Nitro-2-methylpropane	126.5°
1-Nitropropane	131.6°

From the similarity of boiling points of the possible impurities, it seems impossible to obtain a pure grade of chloronitroethane and a good grade of the alcohol from commercial material by reaction B of Fig. 1. If the potassium dinitroethane is purified, or the dinitroethane is fractionated, a good grade of DPL can be obtained by the Ter Meer reaction from commercial grade chloronitroethane. These latter two purifications involve potential hazards which make the procedure undesirable for pilot plant study.

The nitroethane used in reaction A, Fig. 1, can be purified by fractionation without too much difficulty. The impurities are illustrated in Table V. A typical mass spectrographic analysis of commercial nitroethane is: nitromethane, 1.2%; nitroethane, 93.8%; nitropropanes, 5.0%; and nitrobutanes, 0.04%.

TABLE VBoiling Points at Atmospheric Pressure

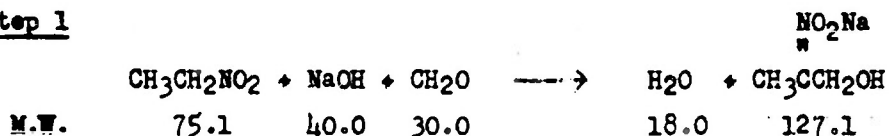
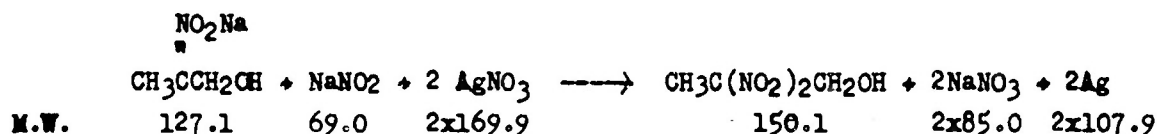
Nitromethane	101°C.
Nitroethane	114°
2-Nitropropane	120°
1-Nitropropane	132°

After fractionation of the commercial nitroethane through a 40-plate column, a typical analysis of the major center portion is: nitromethane, 0.02%; nitroethane, 99.0%; and nitropropanes, 0.98%.

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Because of the purification and hazard involved in the Ter Meer reaction and as the preliminary cost estimates do not favor either process heavily, it was thought that the Shechter-Kaplan procedure was more desirable for pilot plant work. The reactions are:

Step 1Step 22. Ter Meer Experimental Procedure, Laboratory Scale

A stainless steel beaker is set up in an ice bath and is provided with an efficient stirrer. To the beaker are added 110 g. (1.0 mole) purified 1-chloro-1-nitroethane and 300 ml. methanol, and the solution is chilled to 0°C. Add dropwise a solution of 73 g. (1.0 mole) sodium nitrite and 6.6 g. (1.0 mole) potassium hydroxide in 160 ml. water and stir the slurry formed for 2½ hrs., filter while cold. After the yellow potassium dinitroethane precipitate has been washed with cold methanol, it can either be converted to dinitroethane or to dinitropropanol. To prepare dinitroethane the precipitate is returned to the beaker and the ice bath and is slurried with water. The slurry is acidified with 20% sulfuric acid (1.0 equiv.) in the presence of 15 g. of urea at less than 10°C., the solution being brought to a final pH of 3. The oil is separated and that remaining in the water layer extracted with ether to give on distillation at 66°C. (6 mm.), 57.4 g. (0.54 mole, 54%) of colorless 1,1-dinitroethane.

If the dinitropropanol is desired directly, the original methanol washed potassium dinitroethane is returned to the reaction vessel in the ice bath and 500 ml. water, 75 ml. (1.0 mole) 37% formaldehyde solution, and 10 g. urea are added. With stirring, 1 mole of sulfuric acid is added as a 20% solution, dropwise. The reaction solution is then warmed to 45°C. and stirred for 1½ hrs., followed by cooling and extracting twice with 750 ml. portions of ethyl acetate. The ethyl acetate extract is stirred with 1% carbon for an hour, dried over anhydrous sodium sulfate and evaporated. On pulling the resulting oil dry at 60-70°C. with a vacuum pump, 77 g. (0.51 mole, 51%) of waxy dinitropropanol sets to a solid, m.p. 84-87°C. The product has a slight yellow color.

3. Shechter-Kaplan Experimental Procedure, Laboratory Scale

To a vessel equipped with a stirrer are added 150 g. (2.0 mole) of fractionated nitroethane, 340 ml. water, 265 g. ice, and a solution of 88 g.

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(2.1 mole) sodium hydroxide in 176 ml. of water. The ice can be replaced with water and the solution cooled externally. By $\frac{1}{2}$ hr. the nitroethane has gone into solution as the anion and the temperature is below 30°C . After placing the reaction vessel in an ice bath, 149 ml. (2.0 mole) of 37% formaldehyde solution are added slowly from an addition funnel, keeping the temperature below 15°C . This requires about 15 min. and the solution is stirred at 15° to 25°C . for 1 hr. Following this interval, add 150 g. (2.2 mole) of sodium nitrite as a solution in 200 ml. water and stir an additional 15 min.

The reaction is carried out by rapidly adding the prepared salt solution of nitropropanol to 680 g. (4.0 mole) of silver nitrate in a 2 Kg. water solution with the pH adjusted to 6.0 ± 0.2 . The temperature of the reaction is kept less than 25°C . by external cooling or by the addition of ice. The reaction is allowed to proceed for $\frac{1}{2}$ hr. during which time the initial light precipitate turns black, then gray-green; filter. The precipitate is washed twice with 250 ml. of water and the filtrate, which is approximately 2 liters if no ice is added during the reaction, is extracted twice with 1.5 liters of ethyl acetate. The combined extracts are stirred with 1% carbon for 1 hr., filtered with the aid of filter aid, and concentrated at reduced pressure at 50°C . or less. When all the solvent is removed, pull at least 3 mm. of mercury vacuum and gradually raise the temperature of the concentrate. Hold the temperature in the pot at 70° - 75°C . with high vacuum until solidification begins, at which point the product is poured from the flask into a crystallizing dish and dried under vacuum for at least 6 hrs. The dinitropropanol obtained will amount to 210-240 g. (70-80%), have a slight yellow color and a m.p. of 80 - 90°C .

The silver nitrate is recovered from the filter cake with nitric acid in 96 to 98% yield.

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K. 2,2-DINITROPROPYL ACRYLATE (DNPA) PROCESS1. Discussion

The object of this investigation was to develop a pilot plant process for the preparation of DNPA and preferably one in which the produced DNPA does not have to be distilled before polymerization. The DNPA has been prepared previously from DPL and glacial acrylic acid (12), and from DPL and acrylyl chloride (13). With both acrylyl chloride and acrylic acid the reactions were carried out in refluxing benzene and the time required was 4 to 5 days. The product was very dark and had to be distilled. Dr. L. W. Kissinger (13) has used trifluoroacetic anhydride, mole per mole acrylic acid, to remove the water of esterification in a low temperature, short reaction time procedure. This technique gives a very nice product without distillation but the anhydride is very expensive at the present time. The low boiling point of the anhydride and the acid, which can be recovered and reconverted with sulfur trioxide, makes recoveries low, 75-80%.

The Navy Ordnance Laboratory has studied and used metal halides (14) as catalysts in the esterification of DPL with acid chlorides. This technique permitted low boiling solvents as chloroform, carbon tetrachloride, ethylene dichloride, or benzene, and short reaction times, 3 hrs. When this technique was used in the preparation of DNPA from acrylyl chloride, more than the theoretical amount of hydrogen chloride had been swept from the reaction flask in 3 hrs. Acrylyl chloride is quite expensive and difficult to prepare and handle; however, for large runs it can be bought at low enough price to make its use attractive.

The acrylyl chloride as obtained contains cuprous chloride as an inhibitor, and is used without purification or removal of the inhibitor. On thorough washing of the DNPA monomer, the inhibitor is removed and no further inhibition is necessary if the monomer is to be used in a few days, or if the monomer is stored in a cold room.

The resulting product is clean enough to polymerize without distillation.

An ester exchange between methyl acrylate and dinitropropanol was run to prepare DNPA using the procedure of Marans and Zelinski (15). After the product had been washed extensively and after the low boiling fractions had been removed by vacuum, there was obtained in 42% yield a material which nitrogen analysis indicated was 47% DNPA in dinitropropanol. The color of the product was dark, indicating a need for distillation before this method could be considered for the preparation of DNPA. The undistilled material would not polymerize.

2. Experimental Procedure Using Trifluoroacetic Anhydride (TFAA)

To a flask equipped with stirrer, reflux condenser, and addition funnel, held in an ice bath, are added 150 g. (1.0 mole) DPL and 75 g. (1.0 mole) of 96% acrylic acid containing inhibitor. After cooling to 0°C., 220 g. (1.05 mole) of TFAA (as obtained from Minnesota Mining and Manufacturing

Company) are added slowly, keeping the temperature below 10°C. When the addition is complete, remove the ice bath and stir until the reaction is at room temperature. Let stand several hours or overnight.

Remove the excess TFAA and the trifluoroacetic acid that is formed at reduced pressure using a dry ice trap. The residue is then poured into an equal quantity of water and extracted with ether. The ether extracts are washed four times with 250 ml. of water, 2% sodium hydroxide solution until the inhibitor is removed, and four more times with water. Dry the washed solution with magnesium or sodium sulfate, stir with 1% carbon, and filter. After removing the ether and pulling dry by pump, there remain 161 g. (0.79 mole; 79%) of a very slightly colored dinitropropyl acrylate.

3. Experimental Procedure Using Acrylyl Chloride (AC)

The 78.0 g. (0.52 mole) of DPL is dissolved in 400 ml. chloroform in a liter flask equipped with stirrer, dropping funnel, and reflux condenser. After 10.3 g. (0.08 mole) of anhydrous aluminum chloride are added, the solution is warmed to the reflux point and 45 g. (0.50 mole) of acrylyl chloride which are dissolved in 100 ml. chloroform are added slowly over an hour. The reaction is stirred and refluxed for three additional hours. The resulting solution is washed well, first with four portions of 200 ml. water, 2% sodium hydroxide solution, water, sodium bisulfite solution, and finally with four more portions of water. To improve the color of the monomer, the chloroform solution is stirred with 1% carbon for 1 hr., allowed to stand over anhydrous sodium sulfate and filtered. After evaporating the chloroform and pulling dry with the vacuum pump at room temperature, there remain 80 g. (0.39 mole; 79%) of DPL which contain only slight color.

L. THE POLYMERIZATION OF DINITROPROPYL ACRYLATE

Due to the insoluble polymer formed by emulsion techniques and the low yields of low molecular weight polymer formed in solution or suspension, the major emphasis of our study on polymerization has been with the bulk or block technique. The catalyst in all cases was methyl amyl ketone peroxide (MAKP). After the monomer with the catalyst has been held in a closed bottle, flushed with nitrogen, for the required time, the resulting solid polymer is dissolved in a volume (in ml.) of acetone numerically equal to twice the weight of the original monomer in grams. The polymer is precipitated by pouring the acetone solution into twice its volume of methanol or ethanol. The polymer is removed and dried at 50°C. in a vacuum oven.

It was expected that the amount of solvent used to dissolve the raw polymer and the amount of methanol or ethanol used to precipitate it would influence the recovery and properties of the final polymer. Two series of tests were made to determine these effects.

TABLE VI

Varying Amounts of Solvent; Alcohol to Solution Ratio Constant.

<u>Dry Polymer</u>	<u>Acetone</u>	<u>Methanol</u>	<u>Recovery</u>	<u>$\eta_r^{2\%}$</u>
16 g.	19 g.	75 ml.	97%	2.05
16	26	90	94	2.09
16	42	125	99	2.08
16	54	150	92	2.09
<u>Ethanol</u>				
16	19	75	98	2.09

TABLE VII

Varying Amounts of Alcohol; Acetone-Polymer Ratio Constant.

<u>Dry Polymer</u>	<u>Acetone</u>	<u>Methanol</u>	<u>Recovery</u>	<u>$\eta_r^{2\%}$</u>
14 g.	36 g.	75 ml.	65%	2.10
14	36	100	89	2.08
14	36	150	91	2.02
<u>Ethanol</u>				
14	36	150	99	2.21

It can be concluded from these tests that the procedure being used is satisfactory. That is, dissolve the polymer in a minimum convenient quantity of acetone, usually two milliliters per gram polymer, and precipitate the polymer in two or three volumes of ethanol.

Table VIII tabulates some runs made in which poly DNPA was prepared from undistilled monomer from various batches. Varying conditions of polymerization vary the properties of the polymer in the predicted manner. A relative viscosity of a 2% (w/v) solution of 3.0 or higher indicates a polymer of acceptable molecular weight. The conditions that seem to give an acceptable polymer are 0.25% MAKP catalyst, and a polymerization temperature, at least initially, of 40-50°C. Higher temperatures and catalyst concentrations lower the molecular weight of the resulting polymer.

Figure 5 (Appendix B) is a plot of relative viscosity of a 2% solution (w/v) of unwashed polymer in acetone against time of polymerization in hours. The three intermediate points are on a straight line, indicating an induction period of several hours. Under the conditions of the test, the polymerization should have approached its maximum in 60 hrs.

TABLE VIII

Sample	MAKP	Conditions	Relative Viscosity
			$\left(\frac{\text{Viscosity of solution}}{\text{Viscosity of solvent}} \right)$ at 25°C., 2% soln.
387R	1.0%	25°C., 96 hr.; 45°C., 63 hr.	1.45
387SG	"	" " " "	6.40
392SG	"	" " " "	1.50
392R	"	" " " "	1.51
306RR	"	25°C., 40 hr.; 45°C., 50 hr.; 65°C., 90 hr.	1.86
306R	"	" " " "	1.67
306R	0.5%	" " " "	1.82
313R	"	48°C., 40 hr.; 40°C., 6 hr.	1.29
313RC	"	48°C., 40 hr.; 90°C., 6 hr.; 75°C., 16 hr.	1.29
316R	0.2%	48°C., 48 hr.; 58°C., 48 hr.	1.98
320R	0.5%	3 weeks in sunlight, R.T.	2.98
320RA	None	" " " " " Very slight polymerization	
321R ^a	0.25%	45°C., 89 hr.	2.69
324R	"	R.T., 16 hr.; 43°C., 72 hr.	1.94
325R	"	" " " "	6.10
327R1	"	42°C., 65 hr.	3.60
327R2	"	" " " "	4.50
327R4 ^b	"	42°C., 40 hr.; 54°C., 24 hr.	19.40
331R ^c	"	40°C., 42 hr.; 50°C., 24 hr.; 65°C., 8 hr.	4.47
332R	"	42°C., 76 hr.	3.76
332SG	"	" " " "	3.72

a - 133 g. sample polymerized in stainless steel cell, 2 in. long x 2 in. diameter

b - 399 g. " " " " " " " " 6 1/2 in. " x 2 in. "

c - 409 g. " " " " " " " " 6 1/2 in. " x 2 in. "

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1. Cost Estimate for 2-Nitro-1,3-propanediol
Basis: 50 lb. per 12 hr., 45% yield

<u>Material</u>	<u>Moles</u>	<u>Weight (lb.)</u>	<u>Price Per Pound</u>	<u>Total Cost</u>
Formaldehyde (37%)	2.0	60	\$.07	\$ 4.20
Nitromethane	1.0	61	.25	15.25
Sodium hydroxide	1.0	40	.0335	1.34
Sulfuric acid	0.5	50	.03	1.50
Urea	0.25	15	.06	.90
Butanol (loss)		40	.15	<u>6.00</u>
Total Material				\$29.19
Labor for two operators and supervision at \$5.10/hr. for 12 hr.				61.20
Utilities				8.94
Overhead at 25%				<u>24.86</u>
Total				\$124.19
Cost per pound				\$2.48

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2. Cost Estimate for 2,2-Dinitropropane Prepared by the
Shechter-Kaplan Reaction

Basis: 89% Yield on 0.176 lb. mole runs.
2.0% Loss of silver nitrate

<u>Material</u>	<u>Moles</u>	<u>Weight (lb.)</u>	<u>Price Per Pound</u>	<u>Total Cost</u>
2-Nitropropane	0.179	16.0	\$.25	\$ 4.00
Sodium hydroxide	0.183	7.7	.0335	.25
Sodium nitrite	0.183	13.2	.0875	1.16
Silver nitrate	0.352	60.0		
2% loss		1.20	9.00	10.80
Nitric acid	0.472	29.7		
50 lb. of 60% soln.			.05	<u>2.50</u>
		Total		\$18.71
Labor for 11 hr. at \$5.10/hr.				56.10
Utilities				7.48
Overhead (25%)				<u>20.56</u>
		Total		\$102.85
		Cost per pound		\$4.90

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3. Cost Estimate for 4,4-Dinitroheptanedioic Acid

Basis: 0.15 lb.-mole, 36% yield.
13.5 lbs. per batch

<u>Material</u>	<u>Moles</u>	<u>Weight (lb.)</u>	<u>Price Per Pound</u>	<u>Total Cost</u>
Nitromethane	0.15	9.2	\$0.25	\$ 2.30
Sodium hydroxide	0.31	12.6	.0335	.43
Formaldehyde	0.30	9.0	.07	.63
Sodium nitrite	0.16	11.4	.09	1.03
Silver nitrate	0.30	51.0		
Loss 2%		1.02	9.00	9.18
Methyl acrylate	0.38	33.0	.60	19.80
Hydrochloric acid (conc.)		20.0	.05	1.00
Nitric acid (conc.)	0.43	45.0	.055	<u>2.48</u>
Total Materials				\$36.85
Labor for two operators and supervision 20 hrs. at \$5.10/hr.				102.00
Utilities				13.38
Overhead (25%)				<u>38.18</u>
Total				\$190.91
Cost per pound				\$14.15

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4. Cost Estimate for 2,2-Dinitro-1,3-propanediol

Basis: 0.30 lb.-mole; 50% yield or 25.0 lb.

<u>Material</u>	<u>Mole</u>	<u>Weight (lb.)</u>	<u>Price Per Pound</u>	<u>Total Cost</u>
Nitromethane	0.30	18.4	\$0.25	\$ 4.60
Formaldehyde	0.60	18.0	.07	1.26
Sodium hydroxide	0.33	13.2	.034	.45
Sodium nitrite	0.33	22.8	.09	2.05
Nitric acid (conc.)	0.80	84.0 (60% sol.)	.055	4.62
Silver nitrate	0.60	102.0		
Loss 3%		3.06	9.00	27.54
Isopropyl acetate loss		106.0	.12	12.70
Ethylene dichloride loss		24.0	.12	<u>2.88</u>
Total for Material				\$56.10
24 Hrs. labor at \$5.10 per hour				122.40
Utilities				17.85
Overhead (25%)				<u>49.09</u>
Total				\$245.44
Cost per pound				9.80

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5. Cost Estimate for 2,2-Dinitropropanol by Shechter-Kaplan Reaction

Basis: 0.50 lb.-mole run; 60% yield or 45 lb.

<u>Material</u>	<u>Moles</u>	<u>Weight (lb.)</u>	<u>Price Per Pound</u>	<u>Total Cost</u>
Nitroethane (redistilled)	0.50	37.5	\$.40	\$15.00
Sodium hydroxide	0.50	21.0	.034	.72
Formaldehyde	0.50	15.0	.07	1.05
Sodium nitrite	0.55	38.0	.09	3.42
Silver nitrate	1.00	170.0		
Loss 3%		5.1	9.00	45.90
Ethyl acetate loss		200.0	.12	24.00
Nitric acid	1.40	147.0 (60% sol.)	.055	8.10
		Total for material		\$98.19
Labor for 24 hrs. at \$5.10/hr.				122.40
Utilities				22.06
Overhead (25%)				60.66
		Total		\$303.31
		Cost per pound		\$6.74

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6. Cost Estimate for 2,2-Dinitropropanol by Ter Meer Reaction

Basis: 0.50 lb.-mole run; 50% yield or 37.5 lb.

<u>Material</u>	<u>Moles</u>	<u>Weight (lb.)</u>	<u>Price Per Pound</u>	<u>Total Cost</u>
1-Chloro-1-nitroethane (specially purified)	0.50	54.8	.50	\$27.40
Potassium hydroxide	0.50	28.0	.10	2.80
Sodium nitrite	0.55	38.0	.09	3.42
Formaldehyde	0.50	15.0	.07	1.05
Sulfuric acid	0.25	25.0	.03	.75
Ethyl acetate loss		200.0	.12	<u>24.00</u>
Total for material				\$59.42
Labor for 24 hrs. at \$5.10/hr.				122.40
Utilities				18.18
Overhead at 25%				<u>50.00</u>
Total				\$250.00
Cost per pound				\$6.67

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7. Cost Estimate for Dinitropropyl Acrylate by Two Methods

Basis: 75% yield in both procedures on 0.49 lb.-mole
batch or 75 lbs. DNPA

<u>Material</u>	<u>Moles</u>	<u>Weight (lb.)</u>	<u>Price Per Pound</u>	<u>Cost for Procedure</u>	
				<u>TFAA</u>	<u>AC</u>
DPL	0.50	75.0	\$ 6.74	505.00	505.00
AC	0.49	44.1	10.00		441.00
TFAA	0.49	103.0	15.00		
Less Recovered acid	0.735	84.0	5.00		
		\$1,545.00 - 420.00 = 1,125.00			
Acrylic acid	0.49	35.2	1.50	52.80	
Solvent loss and misc. chemicals				<u>75.00</u>	<u>75.00</u>
			Total	\$1,757.80	\$1,021.00
20 Hrs. labor at \$5.10/hr.				102.00	102.00
Utilities				112.00	112.00
Overhead (20%)				<u>247.00</u>	<u>247.00</u>
			Total	\$2,218.80	\$1,482.00
			Cost per lb.	\$29.60	\$19.75

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8. Cost Estimate for Polymerization of DNPA

Basis: 80% Yield on 100 lb. batches; 80 lbs. washed polymer

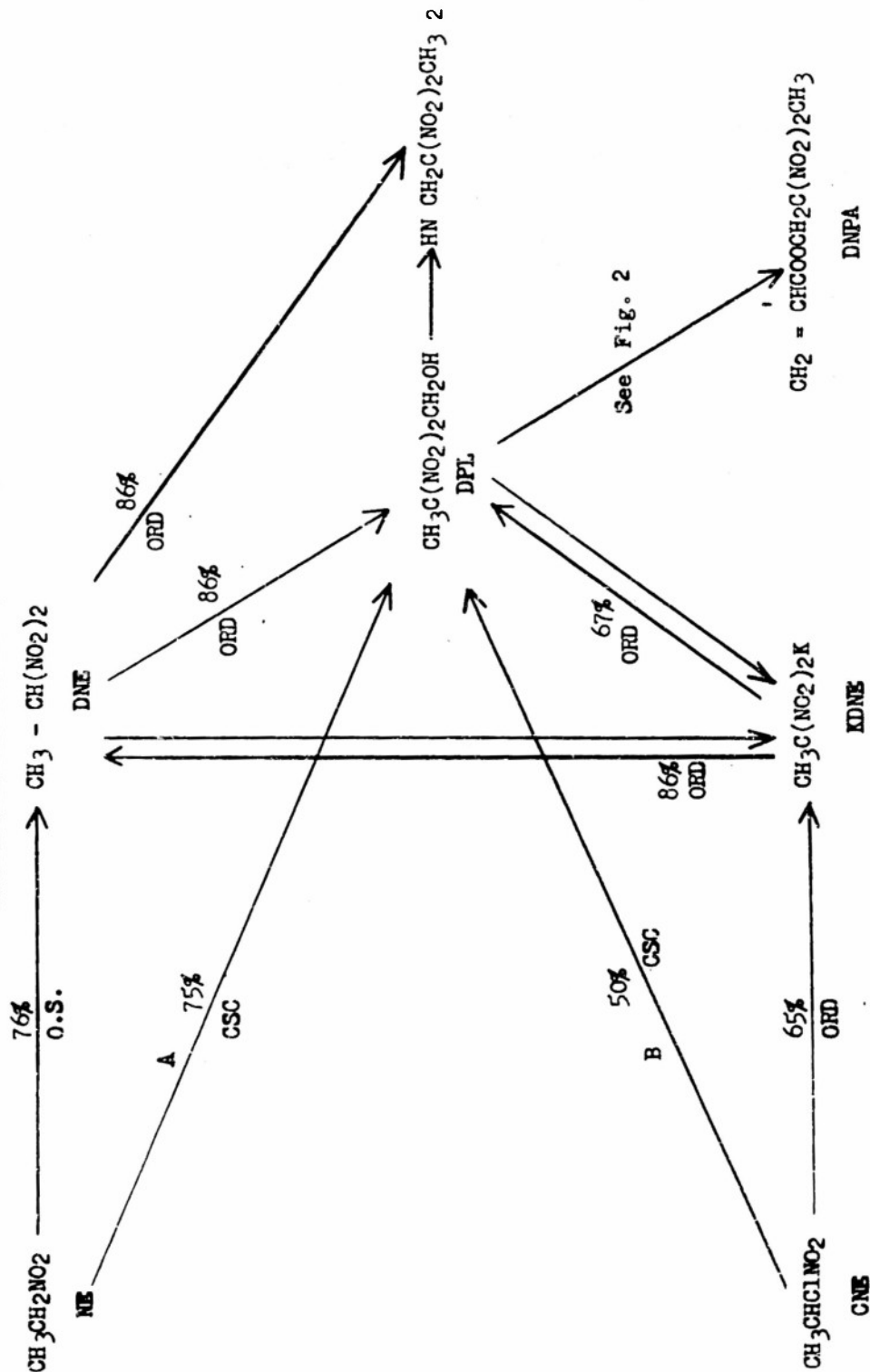
<u>Material</u>	<u>Cost</u>
DNPA 100 lbs. at \$19.75/lb.	\$1,975.00
Solvent loss and catalyst	<u>50.00</u>
Total	\$2,025.00
Labor for 50 hrs. at \$3.05/hr.	152.50
Utilities	108.87
Overhead at 20%	<u>457.20</u>
Total	\$2,743.57
Cost per pound	\$34.35

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APPENDIX B

Fig. 1

Routes to Dinitropropyl Acrylate

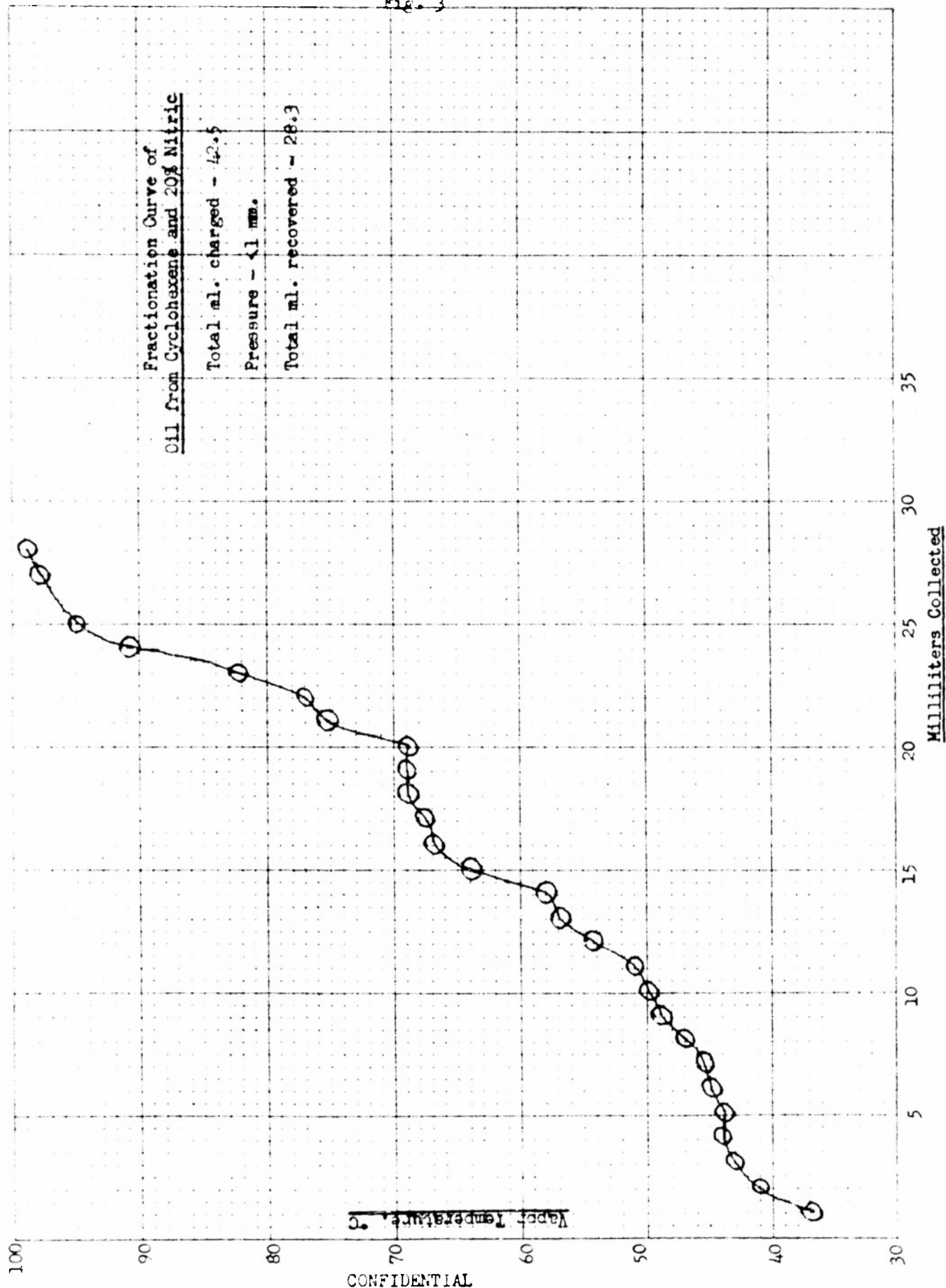


CSC - Commercial Solvents Data
ORD - NAVORD REPORT 2443, June 1952
O.S. - Ohio State Report No. 1, May 1950

APPENDIX BFig. 2Esterification Processes to Dinitropropyl Acrylate

2,2-Dinitropropanol (DPL)	+ acrylyl chloride	[benzene solution Reflux 100 hrs. Distill product 63%	→	2,2-Dinitropropyl- acrylate (DNPA)
	+ acrylyl chloride	[chloroform solution AlCl ₃ catalyst Reflux 3 hrs. Undistilled product 79%	→	
	+ acrylic acid	[benzene solution H ₂ SO ₄ catalyst Reflux 50-65 hrs. Distill product 65%	→	
	+ acrylic acid	[no solvent TFAA condensing agent Requires 6-8 hrs. re- action time Undistilled product 79%	→	

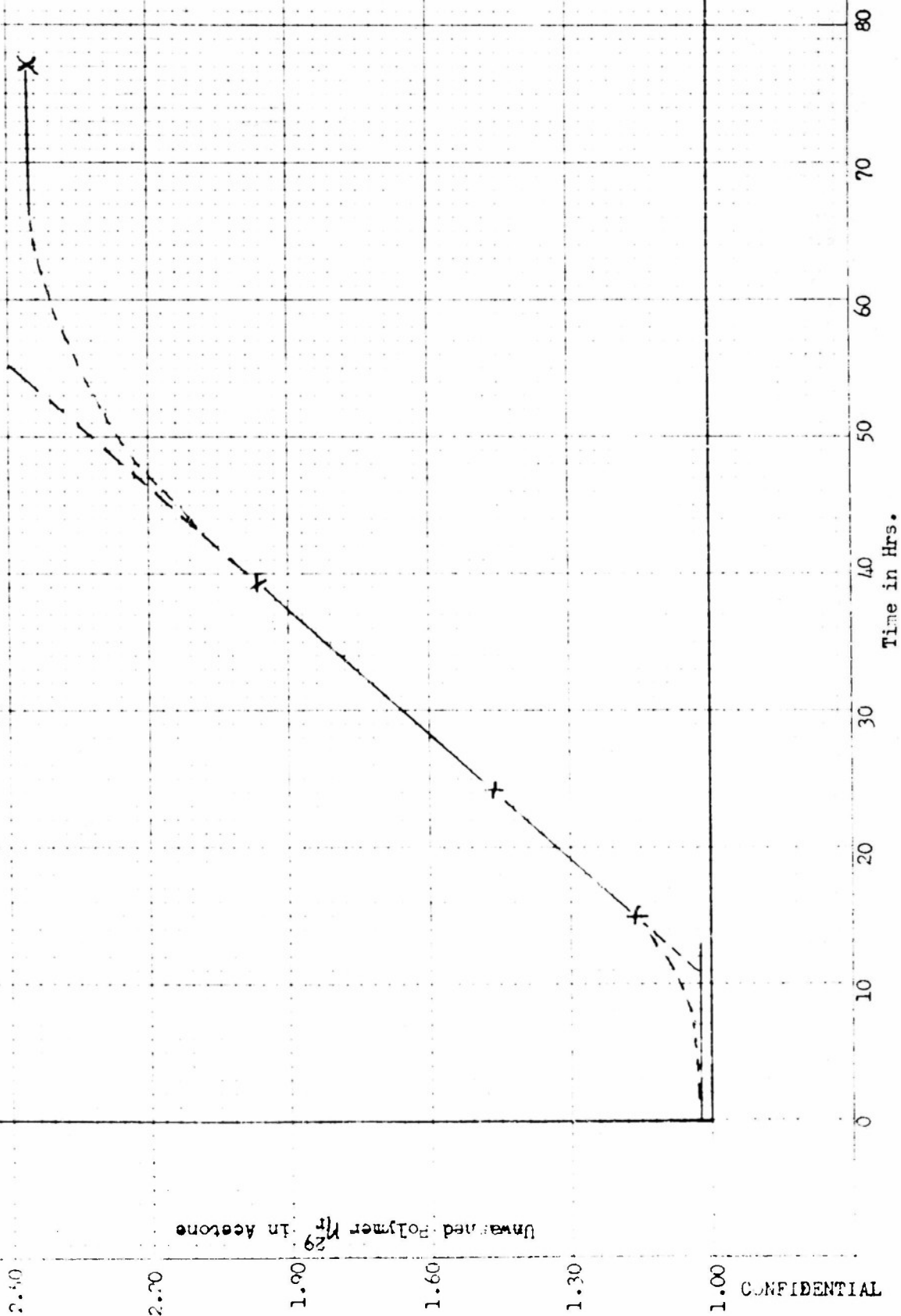
Fig. 3



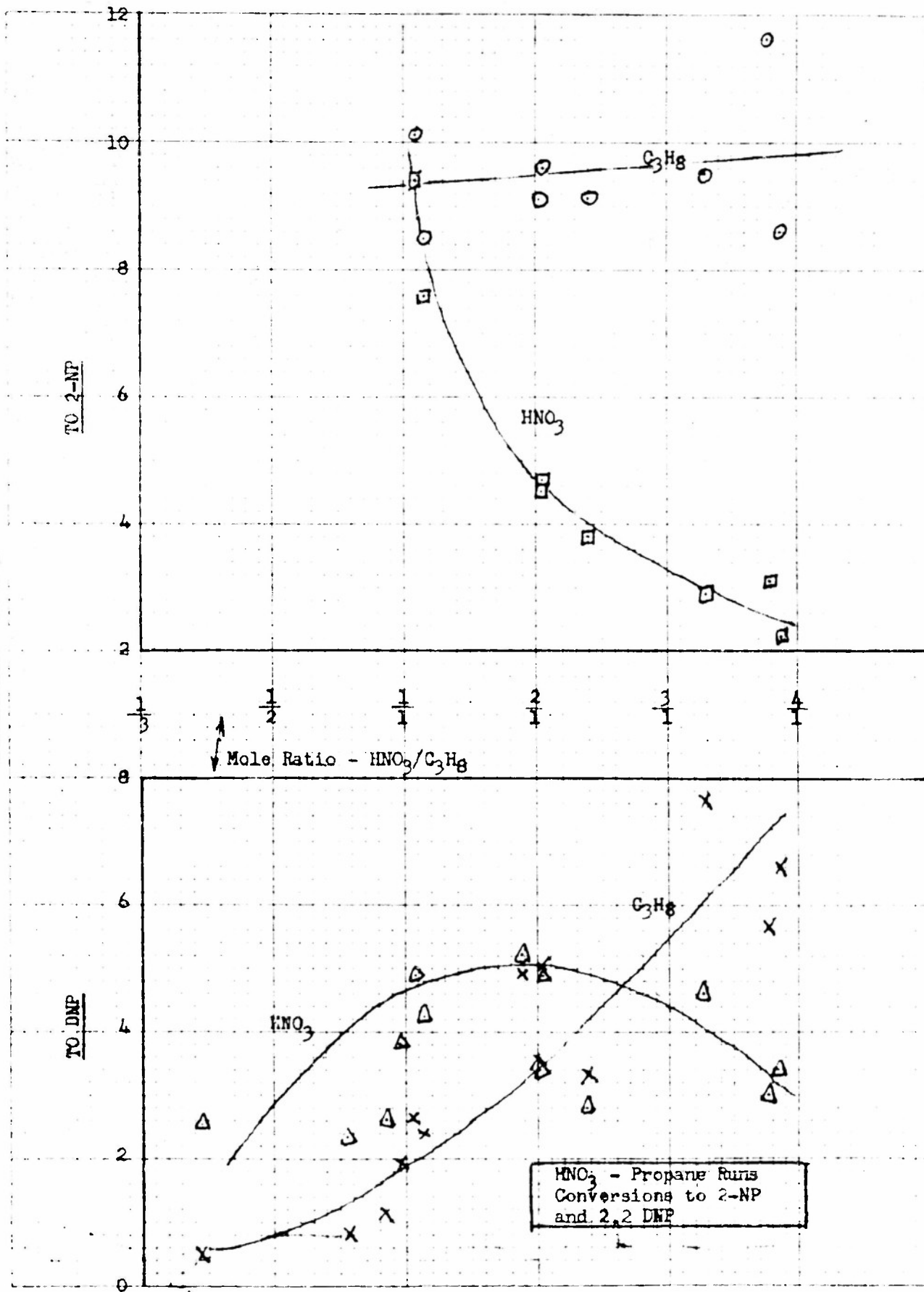
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APPENDIX B
Fig. 4

Rate of Polymerization of DNPA
Catalyst: 0.25% MAKP
Temperature: 43°C.
Method: Mass



APPENDIX B
Fig. 5
CONVERSIONS - MOLE %



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