EFFECT OF VARIATION OF THF, MeOH AND TNT
CONCENTRATIONS FROM OPTIMUM ON YIELD IN
THE CONTINUOUS HNS I SYNTHESIS PROCESS

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DEVELOPMENT DIVISION

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*Normal Process Development
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ABSTRACT

This report covers work accomplished to determine the effect of varying tetrahydrofuran (THF), methanol (MeOH) and trinitrotoluene (TNT) concentrations from pre-established optimums for the continuous HNS I synthesis process. Concentrations were varied $\pm 5\%$ from optimum and synthesis runs were performed using the 1 kg synthesis system. Results were evaluated using crude yield and liquid chromatography analysis as judgment tools. In all cases these deviations from optimum resulted in decreased yields varying from 0.5 to 6.0%.

DISCUSSION

The synthesis of 2,2', 4,4', 6,6 hexanitrostilbene (HNS) involves reacting two separate solutions, (1) sodium hypochlorite (NaOCl) and (2) TNT dissolved in a solvent mixture of THF and MeOH. Optimum concentrations and ratios for a batch process were outlined in a Navy Report(1). These ratios were used as a starting point in the development of a continuous process. The continuous process development effort and the investigative work confirming optimum NaOCl concentration and ratio of the two solutions are detailed in a Mason & Hanger - Silas Mason Co. report(2). The effort described here was undertaken to confirm optimum THF/MeOH/ TNT concentration and to define what effect variations from optimum would have on yield and purity.

Solutions of the three ingredients were prepared at optimum concentration and by varying each solution component $\pm 5\%$ from this optimum. Duplicate synthesis runs were performed for each individual concentration using a 1 kg synthesis system described in an earlier report(3). During these runs the concentration of the NaOCl solution and the ratio of the two solutions involved were maintained at optimum. Thus, the only deviation from a normal synthesis run was in the THF/ MeOH/TNT concentration. The effluent samples from the synthesis runs were allowed to stand at ambient temperature for a minimum period of 18 hours and then washed and slurried to the "crude HNS I" stage. The material was then dried at 100 C for a minimum period of 16 hours, cooled, weighed to determine yield and sampled for liquid chromatography (LC) analysis.

Table I details yield and LC results of the optimum and deviated concentrations. In all cases when deviations from optimum concentrations were employed, the yield decreased. LC results, with the exception of mixtures 2 and 4, indicate that an inferior product is obtained when other

- (1) K. C. Shipp, "Heat Resistive Explosive XVI - A New Synthesis of 2,2', 4,4', 6,6' HNS," (C) NOLTR-64-34 (AD 351283L).
- (2) T. W. Stull, "A Continuous Process for the Synthesis of Hexanitrostilbene," October - December 1975, MHSMP-75-5F.
- (3) T. W. Stull, "Synthesis of High Purity Hexanitrostilbene," September 1975, MHSMP-75-37.

Table I. Percent Yield and Liquid Chromatography Results
of Various THF/MeOH/TNT Mixtures

	<u>THF/MeOH/TNT Mixtures</u>	<u>Yield (%)</u>	<u>% TNB^b</u>	<u>% DPE^c</u>	<u>% HNS</u>
1.	THF 5/MeOH 2.5/TNT 0.5 ^a (Optimum)	44.5	Trace	6.2	93.6
2.	THF 5.25/MeOH 2.5/TNT 0.5 (5% Excess THF)	42.9	Trace	5.6	94.2
3.	THF 4.75/MeOH 2.5/TNT 0.5 (5% Decrease THF)	41.8	0.4	8.0	91.5
4.	THF 5/MeOH 2.625/TNT 0.5 (5% Excess MeOH)	38.4	0.4	4.0	95.5
5.	THF 5/MeOH 2.375/TNT 0.5 (5% Decrease MeOH)	43.0	Trace	8.3	91.5
6.	THF 5/MeOH 2.5/TNT 0.525 (5% Excess TNT)	43.2	0.8	6.6	92.7
7.	THF 5/MeOH 2.5/TNT 0.475 (5% Decrease TNT)	44.3	1.5	5.4	93.0

^aFigures following THF and MeOH are in litres, those following TNT are in kilograms

^bTrinitrobenzene

^cDipicrylethane

than optimum ratios are employed. The scatter of LC results was anticipated due to the difficulty of obtaining a uniform sample of a "crude" product. In the evaluation of test results the most emphasis was placed on yield results due to the fact that the LC results are not absolute and to the accompanying sampling problems.

CONCLUSIONS

In all cases deviation of $\pm 5\%$ from the optimum concentration resulted in lower yields, and generally inferior products. Results of this testing indicate that a deviation of $\pm 1.0\%$ from optimum concentration would be a realistic limit of allowable deviation for the continuous HNS I synthesis process.