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CONTRACT DA-23-072-501-ORD-48
DEVELOPMENT STUDY FOR IMPROVEMENT
OF THE MANUFACTURING PROCESS FOR
TRIETHYLENEGLYCOLDINITRATE (TEGDN)

Prepared For:

U.S. ARMY ORDNANCE CORPS
PICATINNY ARSENAL
DOVER, NEW JERSEY



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Contract Period: March 1960 through December 1960)

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BY

PROPELLEX CHEMICAL DIVISION
CHROMALLOY CORPORATION
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I. OBJECTIVE

The purpose of Contract DA-23-072-501-ORD-48 was to carry out studies which would lead to an improved process for the manufacture of triethyl neglycoldinitrate (TEGDN). The studies were to include literature survey, chemical kinetic considerations, process variables such as temperature, concentration of reactants and reaction times, recovery of spent acid and process economic considerations. The process developed was to be described in detail. General pilot plant equipment design and criteria for material of construction were to be established. An attractive process should -

1. Give adequate separation of product and spent acid phases without diluting the nitrator charge to the extent that recovery of spent acid is not economically feasible.
2. Yield a spent acid which is stable and recoverable.
3. Obtain a yield and purity of product at least comparable to the present process, and acceptable under present requirements.

II. INTRODUCTION

TEGDN has come into prominence as a high energy plasticizer for nitrocellulose and cellulose acetate in rocket solid propellant because of its strong plasticizing property and relative impact insensitivity. In these two respects it is significantly superior to nitroglycerine.

German propellant chemists such as Major General Uto Gallwitz were the first to recognize the value of nitrated glycols in gun and rocket propellants and exploit this advantage in full scale production. In contrast to the catastrophic scarcity of nitroglycerine in Germany in World War I (due to a shortage of glycerine obtained from fats or sugar), by World War II Germany had replaced

nitroglycerine by di and triethyleneglycoldinitrate in gun and rocket propellants. The United States has been slower to shift from nitroglycerine to nitrated glycols as the plasticizer in double base propellant compositions. Therefore, relatively small amounts of pure TEGDN have been manufactured in the United States and practically no research or development has been reported in English on optimizing either the batch or continuous process for preparation of TEGDN. Picatinny Arsenal and the Naval Propellant Plant have manufactured TEGDN.

III. LITERATURE SURVEY

A literature survey was conducted using the following periodicals and texts:

Chemical Abstracts

Journal of the American Chemical Society

Journal of Physical Chemistry

Industrial and Engineering Chemistry

Memorial des poudres et saltpetres (Paris)

Organische Chemie - Beilstein

Unit Processes in Organic Synthesis, Fifth Edition - Groggins, McGraw-Hill (1958)

The Theory of Rate Processes - Glasstone, Laidler and Eyring - McGraw-Hill (1941)

Textbook of Physical Chemistry, Second Edition, Glasstone - D. Van Nostrand (1946)

The Theory of Organic Chemistry, Branch and Calvin - Prentice Hall (1941)

Systematic Inorganic Chemistry of the Fifth and Sixth Group Non-metallic Elements, Yost and Russell - Prentice Hall (1946)

MIL-STD-286 - Military Standards of Propellants Sampling, Inspection and Testing - 28 June 1956

Properties of Explosives of Military Interest - Picatinny Arsenal Report 1740, Rev. 1, Tomlinson and Sheffield

The physical, chemical and explosive properties of TEGDN reported in the literature are listed below. (Lower case letter subscripts refer to the sources listed in Appendix "A"):

Structure: $\text{O}_2\text{NO}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{ONO}_2$ _{a.}

Color and Form: light straw yellow to water white oil

Molecular Weight: 240.172 _{b.}

Density, gm/ml, 16°C.: 1.3291 _{c.}
20°C.: 1.33 _{a.}
22°C.: 1.327 _{d.}
25°C.: 1.32 _{a.}

Melting Point: -19°C. _{a.}

Boiling Point: Decomposes _{b.}

Refractive Index, $n_D^{7.7}$: 1.4596 _{c.}
 $n_D^{17.5}$: 1.4560 _{d.}
 $n_D^{21.2}$: 1.4542 _{c.}

Viscosity, 6.0°C.: 0.257 Poises _{c.}
20.3°C.: 0.119 Poises _{c.}
54.2°C.: 0.0415 Poises _{c.}

Volatility, 60°C., $\mu/\text{cm}^2/\text{hr}$: 40 _{a.}

Impact Sensitivity, 2Kg Wt: _{a.}

B. M. Apparatus: 100+ cm

P. A. Apparatus: 2 in. _{n.}

Friction Pendulum Test: a.

Steel Shoe: Unaffected

Fibre Shoe Unaffected

Explosion Temperature, 5 seconds: 223°C. a.

Heat of Combustion, cal/gm: 3428 a.

Heat of Explosion, cal/gm: 357 a.

Gas Volume, cc/gm: 851 a.

Vapor Pressure, 25°C.: 0.001 mm. Hg a.

Solubility in H₂O, gm/100 gm:

25°C. : 0.55 a; 0.66 c.

60°C. : 0.68 a.

Solubility, other solvents at 25°C.:

Ethyl ether: infinite

Ethyl alcohol: infinite

Acetone: infinite

Methylene chloride: infinite

Hydrolysis, % acid released: a.

After 10 days at 22°C. : 0.032%

After 5 days at 60°C. : 0.029%

The decomposition temperature of TEGDN has been measured by Whittaker_e at one atmosphere and found to be 228°C. Steinberger and Corder_g measured the surface temperature of combustion of TEGDN at 800 psi and found it to be approximately 300°C.

Pristera_n reports a qualitative method for the analysis of ether-soluble constituents of propellants by infra-red spectroscopy. TEGDN was characterized by a peak at 8.85 microns which is characteristic of the adsorption of the —C—O—C— ether bond.

Medard_i investigated the shock sensitivity of liquid nitrate esters and reported that TEGDN was about 8.4% as impact sensitive as nitroglycerine. However, sensitivity to shock is dependent on conditions such as confinement.

The heat of reaction of the nitration of triethylene glycol to yield TEGDN has been calculated_b (See Appendix "B") and found to be 11600 calories/gm-mole of TEGDN formed.

Triethylene glycol was first prepared in 1863 by Leurenco_j, who heated glycol with ethylene bromide to 115-120° in a sealed tube. Wurtz later that year prepared TEG by the epoxy condensation of glycol and ethylene oxide at 100°C._k, and subsequently studied the nitric acid oxidation of the TEG to its corresponding dibasic carboxylic acid. The glycol was nitrated by the Germans_m and Italians in World War II and used as a plasticizing component of double-base rocket and gun propellants.

Tomlinson and Sheffield_a report the following method for the laboratory preparation of TEGDN developed at Picatinny Arsenal.

TEG was purified by fractional distillation under vacuum at a pot temperature of 180°C. and a take-off temperature of 120°C. An eighteen inch Vigreux fractionating column was used with a five to one reflux ratio. The purified TEG was nitrated at 0°C. (+ or - 5°C.) by addition of the glycol to 2.5 parts of 65-35-5 $\text{HNO}_3\text{—H}_2\text{SO}_4\text{—H}_2\text{O}$ nitrating mixed acid. TEG was added at the rate

of 300 gm/40 minutes after which the mixture was held at temperature for another 30 minutes. The nitrating mixture was drowned in ice water and the resulting two-phase system extracted three times with ether. The resulting extract was water washed to a pH of 4. Sodium bicarbonate washes followed by water washes resulted in a nearly neutral ethereal extract. The ethereal solution was dried over calcium chloride and the ether removed by bubbling with dried air. The yield reported was 84% of theoretical with a nitrometer nitrogen analysis of from 11.60 to 11.69% (calculated 11.67%).

Aubertein discussed optimum mixed acid compositions, ratios, and reaction times for a number of nitrated glycols. He found that the H_2SO_4 lowered the solubility of the nitrate in the nitration bath and thereby increased yields. However, sulfation, while slower than nitration, was sufficiently rapid so that yields went through a maximum with time and then fell off due to sulfation losses. Aubertein also reported that an increase of H_2SO_4 also increased the separation time, lowered the HNO_3 content of the product and decreased the stability of the mixed acid. Sulfuric acid attacked TEGDN to give unstable sulfate esters.

He reported that increasing the total mixed acid increased the degree of nitration and solubility loss with an optimum amount for maximum yield, increased mixed acid stability, promoted separation, and increased the HNO_3 content of the product.

Most of Aubertein's nitrations were run at 20°C. For the addition of 75 grams of TEG to 185 grams of mixed acid, a typical cycle required .2 minutes

for addition with two more minutes for agitation and reaction. He reported no advantage to drowning before separation. The product was found to be 40% (alc) HNO_3 in the case of TEGDN. This HNO_3 went into the first wash water which was a 15-20% H_2SO_4 solution. Aubertein found the spent acids too unstable for storage and recommended immediate and preferably continuous denitration.

Aubertein's mixed acid for TEGDN had the following compositions: HNO_3 : 70%; H_2SO_4 : 28+%; H_2O : less than 2%. His nitration ratios were 75 grams TEG to 185 grams mixed acid or one part glycol to 2.47 parts mixed acid. From this reaction he reported a yield of 86%.

It is reported₁ that Picatinny Arsenal has investigated processes for the manufacture of TEGDN using a nitric acid/sulfuric acid ratio of 75/25 with a nitric acid/TEG ratio of 2/1. Picatinny Arsenal found that increasing the nitric acid decreased the solubility of the TEGDN in the nitrating bath and increased the spent acid stability. They reported that diluting the spent acid with an equal volume of 95% sulfuric acid resulted in markedly increased stability of the spent acid. Similarly, dilution of the spent acid with nitroglycerine spent acid (which is higher in sulfuric acid) resulted in a more stable spent acid. Drowning of the above nitration bath and neutralization before separation resulted in a reported 95% yield.

It has been reported₁ that some British workers have found a 70/30 nitric acid/sulfuric acid ratio with one part TEG to 2.5 parts of acid as the reaction ratio gives good separation and a spent acid which is stable for 1.75 hours at 25°C.

These workers found that the stability of diethylene glycol dinitrate spent acids decreased with the use of impure DEG. Where the water content of the spent acid was 26.5%, the highest usual value, the stability at 20°C. was for from 3 to 4 hours. Adding nitric or sulfuric acid to the spent acid to reduce the water content to 20% increased the stability to 24 hours at 20°C.

IV. EXPERIMENTAL WORK

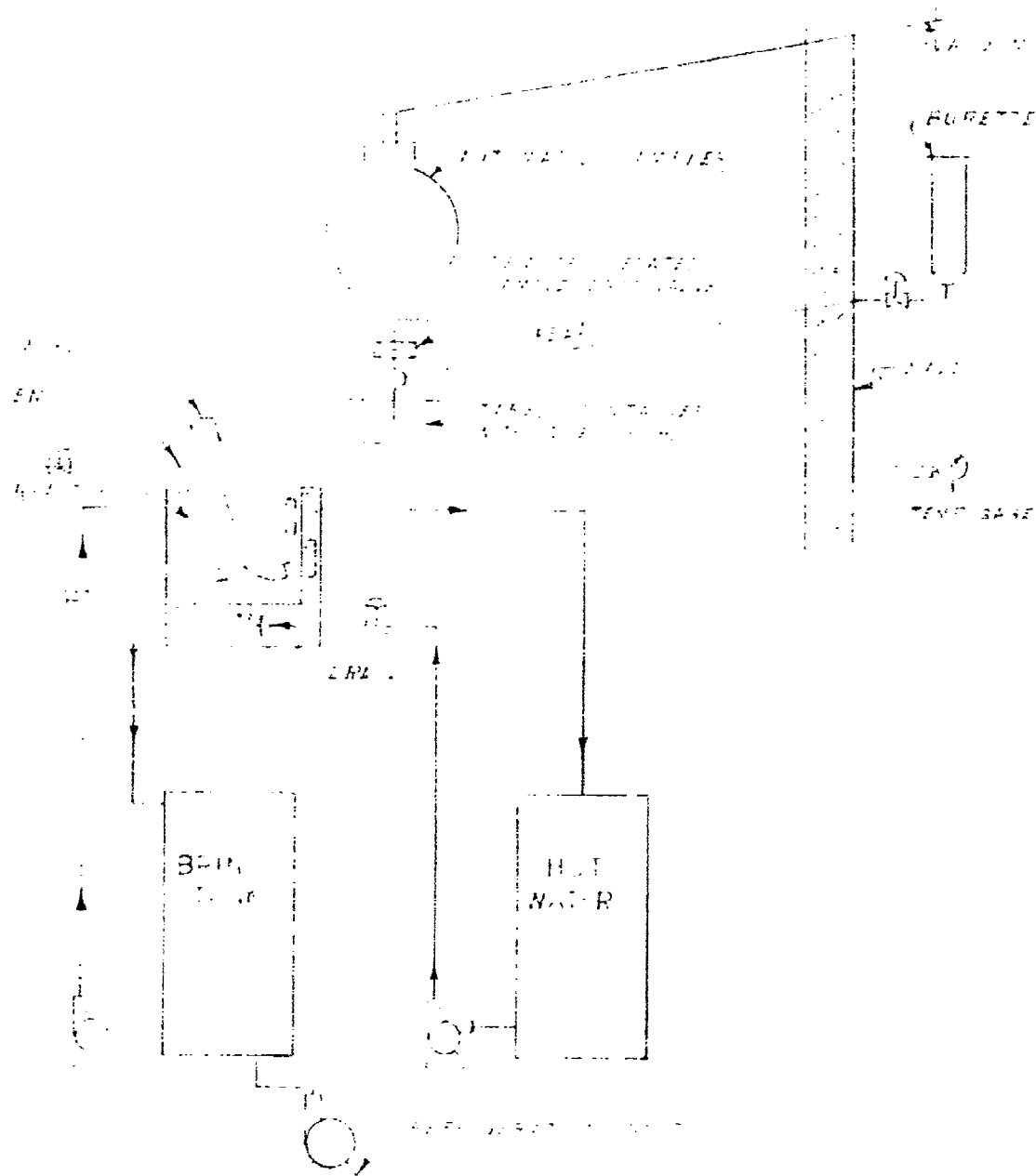
A. Apparatus Design

A versatile nitration apparatus for the study of the TEGDN reaction was designed and built with due consideration of the explosive hazards. A schematic diagram of this apparatus is shown in Figure 1.

The reactor consists of an interchangeable stainless steel beaker with a quarter inch pipe welded to the bottom. Reactors of the following capacities were used: 500 ml, 1000 ml, 1500 ml. The reactor sets in a larger brine jacket which cools the reaction. This jacket connects with a larger (approximately 25 gallon) brine reservoir which is cooled by a one-third H.P. compressor to -20°C . A secondary hot water coil in the brine tank is fed by a hot water reservoir held at 175°F . and this system is used to modify the temperature of the brine system to insure closer temperature control. Thermocouples indicate the temperatures of the reaction mixture, the brine tank, the hot water reservoir and the brine reservoir.

Triethylene glycol is metered into the reactor through a tube by gravity flow. The reservoir for the glycol is a burette on the operator's side of a protective wall. The flow rate of glycol can be closely controlled by the operator peering through an explosion-proof port. The reactor may be flooded in an emergency.

At the conclusion of a reaction, the reaction mixture is transferred by gravity flow to a refrigerated separatory funnel equipped with a solenoid stainless steel valve so that separation of the product layer may be accomplished remotely.



SCHEMATIC DIAGRAM
EXPERIMENTAL NITRATION ARRANGEMENT

For the kinetic study sampling of the reacting system at various times was necessary. This was accomplished remotely by the use of an automatic chromatographic table which has been modified for this work.

Figure 2 is a photograph of the nitration apparatus. The circular table in the center of the photo is an automatic chromatograph column sampler which has been modified to allow automatic sampling of the reaction mixture at short intervals.

Figure 3 is a close-up of the reactor proper, showing how the stainless steel reaction pot may be removed from the brine tank and another reactor substituted. The refrigerated separation funnel with its solenoid-actuated valve is seen on the left of the photo.

When a sample is taken, vacuum is applied to a separatory funnel, pulling a sample from the reactor. When the vacuum is broken, the sample column is returned to the reactor. The separatory funnel holding the sample is equipped with a solenoid stainless steel valve which activates to release the sample into a tared container of quench water. This halts the reaction while giving an accurate weight of the sample taken. A new tared container of quench water is then automatically rotated into place for the next sample. By this method samples may be easily taken at one minute intervals.

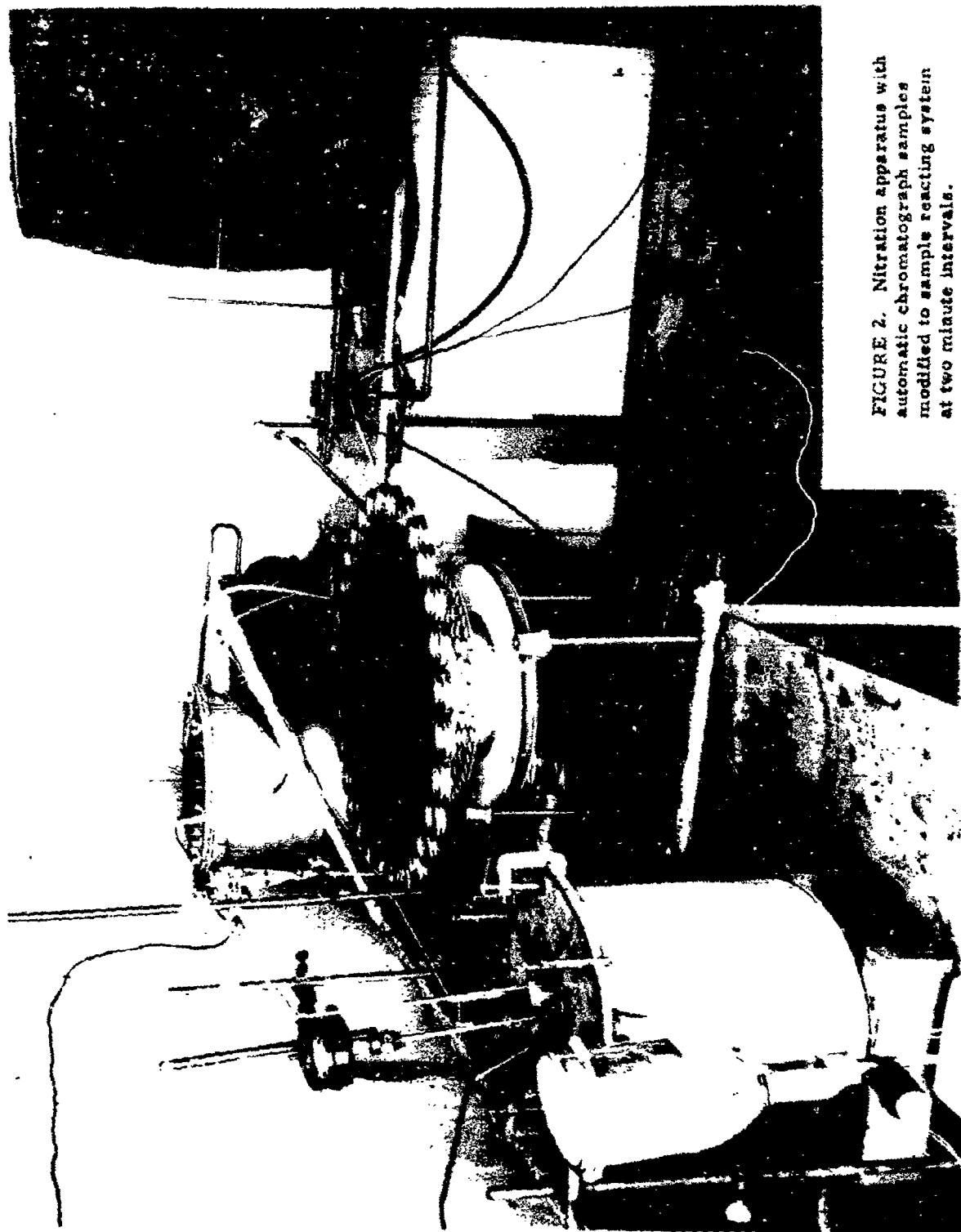


FIGURE 2. Nitration apparatus with automatic chromatograph samples modified to sample reacting system at two minute intervals.

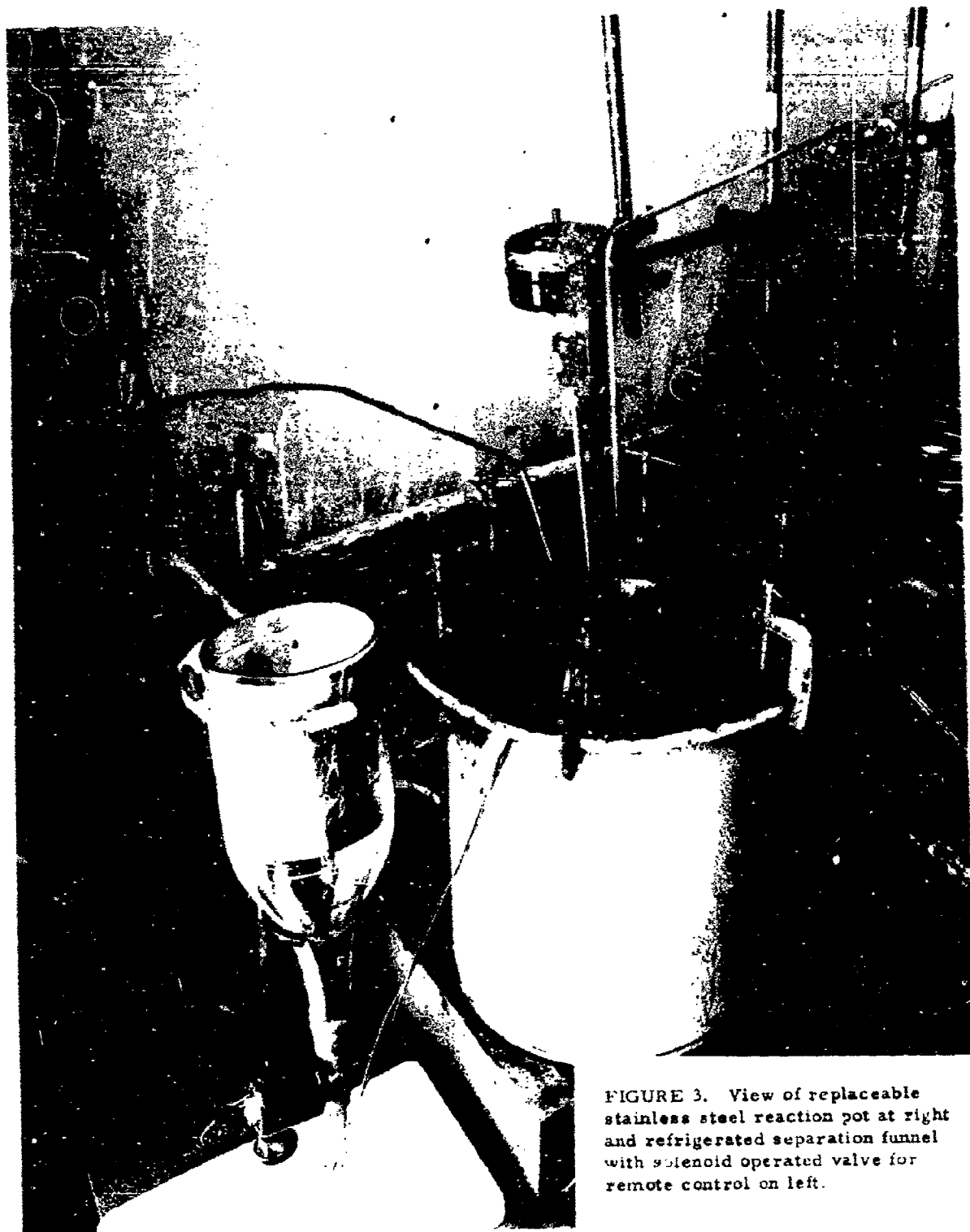


FIGURE 3. View of replaceable stainless steel reaction pot at right and refrigerated separation funnel with solenoid operated valve for remote control on left.

B. Chemical Kinetics Study

The work on this phase began with an exploration of systems with reactant concentrations close to those described by Aubertein₂ as optimum for the production of TEGDN. No attempt was made during these early familiarization runs to collect time samples to study the kinetics of the reaction. The reagent grade acids used were assayed against standard sodium hydroxide which had previously been standardized using phenolphthalein against potassium acid phthalate primary standard.

Initially, the 93.4% nitric acid and 94.5% sulfuric acid were used to prepare 175 grams of a mixed acid containing 70% HNO_3 and 30% H_2SO_4 . No attempt was made initially to adjust for water in the acid to assure the maximum of 2% H_2O specified by Aubertein. As a result, the actual mixed acid composition was:

HNO_3	:	65.38%
H_2SO_4	:	28.35%
H_2O	:	6.2%

This reaction was run at -5°C . with good control. Seventy-five (75) grams of TEG was added to the reactor over 22 minutes and agitation continued for fifteen minutes after addition of final TEG. The reaction, however, had to be drowned during separation because of a fume-off.

The reaction was run again under the same conditions. The separated TEGDN layer was washed four times with 10% sodium bicarbonate, water washed twice and dried under vacuum at 60°C . The crude yield was 36.2%.

A similar reaction was run at 0°C . and the separated layer treated identically. This time the yield increased to 48.5%.

In four nitrations, #1, 2, 3 and 4, the reaction was sampled periodically during the hold period (i.e. after the addition of all the triethylene glycol), in an attempt to collect kinetic data for rate determinations. Of this group the first nitration run was lost because of fume-off. Yield data as a function of time was collected on all of the other runs.

Nitrations #2, #3 and #4 were sampled for kinetic data. Nitration #2 was conducted at a temperature level of 0 C., nitration #3 at -15°C., and nitration #4 at +10 C. The reactor was charged with mixed acid and the triethylene glycol was metered into the reactor with agitation. Since Aubertein^d had noted a decrease in yield with increased reaction and hold time because of the decomposition of the nitrate and the formation of the sulfated glycol, it was decided to hold the addition period to as low as practicable with existing refrigeration equipment. Previous experience indicated that most additions could be completed by the end of fifteen minutes. It subsequently developed that this was a reasonable period of addition for all except the very low temperatures.

The addition of the glycol was completed in fourteen minutes in nitrations #2 and #4 but nitration #3, because of the very low reaction temperature of -15 C., required 70 minutes for addition. Nitration #2 was sampled every five minutes after the addition of the glycol; nitrations #3 and #4 were sampled every three minutes.

A series of tared beakers, filled with quench water, were placed in the circular rack of the automatic sampler. At the proper moment a sample was drawn from the reactor by opening a remote vacuum line. This caused an

estimated fifteen grams of the reaction mixture (which was highly emulsified through agitation) to be drawn into a separatory funnel, equipped with a solenoid valve. As soon as the siphon column was broken and the residue discharged into the reactor, the solenoid valve dropped the sample into a tared beaker of quench water and the sample table rotated another beaker into place under the separatory funnel. Subsequently, these beakers were weighed to determine the exact weight of the sample drawn and their contents were titrated with standardized NaOH to determine the free acid per gram of sample and, by difference, the amount of TEGDN formed. The method of calculation is shown at the bottom of Table I.

The kinetic data on nitrations #2, #3 and #4 are given in Table I and Figure 4. Because of the low temperature of -15°C . at which nitration #3 was conducted, a temperature which was at the lower limit of the brine system of the experimental reactor, seventy minutes were required for the addition of all of the glycol. Even at this low temperature, however, the reaction appeared to be complete at nine minutes after the addition of the last of the glycol. (In all of these reactions, no attempt was made to determine degree of sulfation by any quantitative technique).

The kinetic data for nitrations #2, #3 and #4 have been reduced and plotted in Figure 4, assuming that all acid loss is due to the formation of TEGDN and that no acid is lost to sulfated triethyleneglycol.

It should be noted in Table I and Figure 4 that the reaction proceeds at such a rate that essential equilibrium is reached in within six to eleven minutes after final addition, at temperatures of from -15°C . to $+10^{\circ}\text{C}$.

The concentrations of TEGDN calculated by this (kinetic study) method are somewhat higher than the actual yields, so it is apparent that some side reaction such as sulfation was taking place. thus it is reasonable to assume that the nitration reaction was complete in less time than shown in these data.

A new and different technique would be required to determine these reaction rates with greater accuracy.

TABLE I

CHEMICAL KINETIC DATA, NITRATION RUNS #2, #3 & #4

NITRATION #2 0°C.				NITRATION #3 -15°C.				NITRATION #4 +10°C.			
1	2	3	4	1	2	3	4	1	2	3	4
Time Min.	Acid conc	Drop in Acid conc	TEGDM conc gms/gm	Time Min.	Acid conc	Drop in Acid conc	TEGDM conc gms/gm	Time Min.	Acid conc	Drop in Acid conc	TEGDM conc gms/gm
*	11.98	-	-	*	12.10	-	-	*	12.50	-	-
0	-	-	-	0	8.94	3.16	.379	1	8.92	3.58	.430
5	8.36	3.62	.434	3	8.56	3.54	.425	4	8.38	4.12	.494
10	8.32	3.66	.439	6	8.58	3.52	.423	7	8.46	4.04	.485
15	8.30	3.68	.442	9	8.48	3.62	.435	10	8.32	4.18	.501
20	8.13	3.85	.462	12	8.53	3.57	.428	13	8.46	4.04	.485
25	8.10	3.88	.466	15	8.50	3.60	.432	16	8.50	4.00	.480
30	8.05	3.93	.472	18	8.48	3.62	.435	19	8.43	4.07	.488
35	8.10	3.88	.466	21	8.50	3.60	.432	22	8.40	4.10	.492
40	8.09	3.89	.467	24	8.45	3.65	.438	25	8.30	4.20	.504
45	7.96	4.02	.482	27	8.50	3.60	.432	28	8.34	4.16	.500
50	7.88	4.10	.492	30	8.41	3.69	.443	31	8.49	4.01	.481
55	7.97	4.01	.481	33	8.48	3.62	.435	34	8.40	4.10	.492

NOTES

1. Column 1. Elapsed time in minutes from addition of last of TEG to taking of kinetic sample. * indicates start of reaction.
2. Column 2. Acid concentration in mille-equivalents (m.e.) per gram of reaction mass. Top figure is concentration before reaction starts based on all acid and TEG being in reactor at start. Acidity at start of reaction determined by NaOH titer of sample of mixed acid and calculation to concentration in m.e./gm of expected total reaction mass. Thus, $\frac{\text{ml} \times \text{N of NaOH} \times \text{gms M.A. in reactor}}{\text{gms M.A.} + \text{TEG in reactor}} = \text{m.e./gm in reactor}$, at start of reaction. Acidity, in reactor, at any time determined by titer of sample: $\text{ml} \times \text{N/gm reactor sample} = \text{acid conc. in m.e./gm in reactor}$.
3. Column 3. Drop in acid from starting concentration to that existing at time of kinetic sample, units are m.e./gm of reaction mass.
4. Column 4. TEGDM concentration, in grams per gram reaction mass, due to conversion of HNO_3 to TEGDM.

Calculation: Mol wt TEGDM = 240.17; equivalent wt = 120.08 gms
 Mille equivalent wt = .12008 gm
 Acid concentration drop due to reaction, forming
 TEGDM in m.e. (Col. 3) \times m.e. wt. TEGDM = gms TEGDM/gm
 in reactor. Therefore, drop in m.e. acid/gm \times .120 = TEGDM
 gm/gm in reactor.

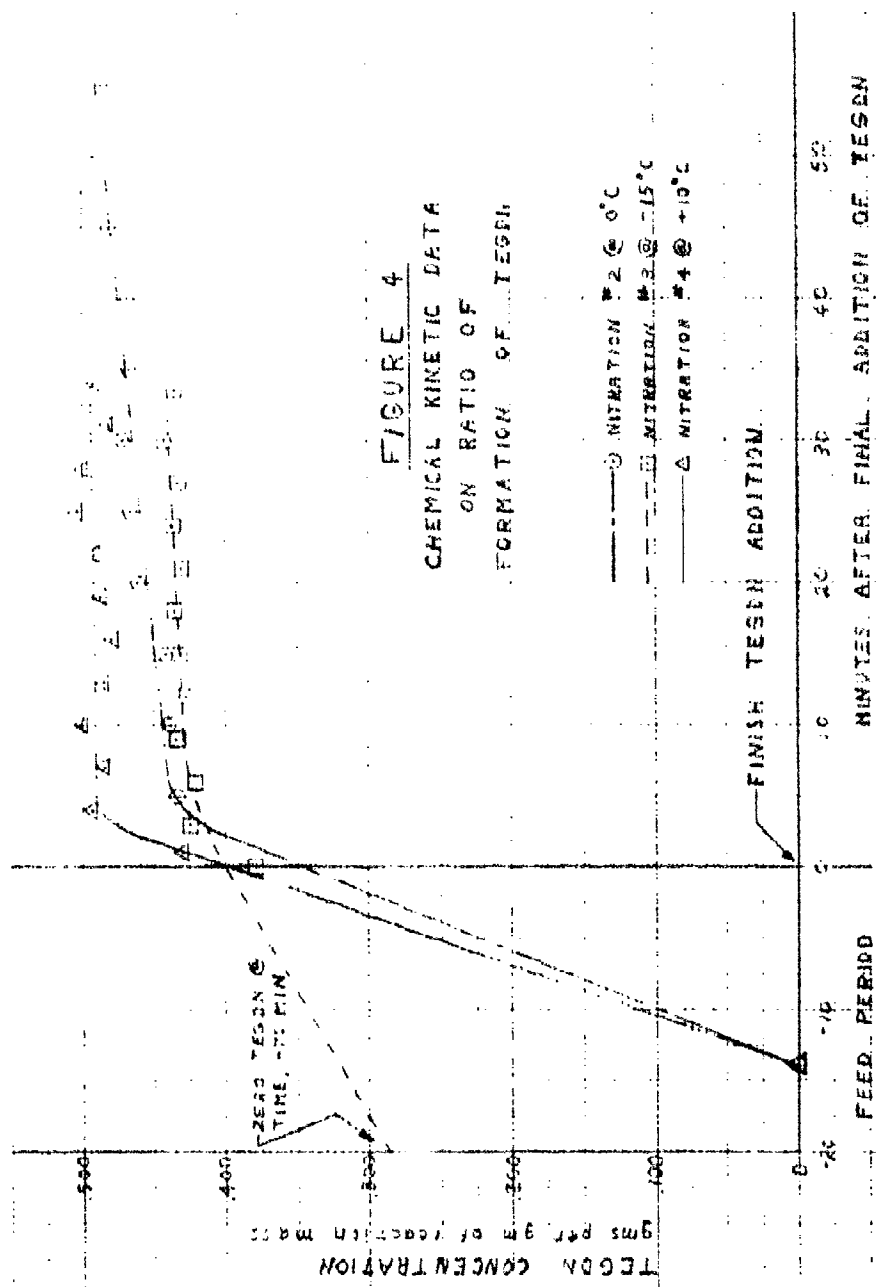


FIGURE 4
CHEMICAL KINETIC DATA
ON RATIO OF
FORMATION OF TEGON

No great difficulty was noted in a solventless nitration.

Samples of the reaction mixture taken for analysis and observation were often found to be deep green in color but on standing reverted to a straw color.

Little difficulty has been experienced in separating product and acid layers without quenching except in the case of nitration #8. This seems to stem in large part from the temperature control of the separatory funnel used. This funnel is refrigerated by a coil immersed directly in the reaction mixture. Generally, 0°C. is chosen as a target temperature for separation, although higher temperatures have been used successfully.

The method used for assay is a modification of Methods 208.1.2, the method for nitroglycerine, in MIL-STD-286 "Military Standard - Propellants: Sampling, Inspecting and Testing" dated 28 June 1956. We use a factor of 4.0003 for TEGDN, instead of 2.523 as used for NG.

Some anomalous yield results were obtained although not recorded in Table IV; attempts to duplicate run 11 resulted in yields ranging from 48% to 80%. It was noted that the relative humidity during this period was greater than 95%. An experimental determination of the weight increase of a sample of sulfuric acid agitated in the nitrator for one hour was made and the sulfuric acid was found to have absorbed over eight per cent of its own weight in atmospheric moisture. As a result of this experiment, the nitrator was modified so that nitrations could be carried out in an atmosphere of dry carbon-dioxide or nitrogen. No further inconsistencies were found after this modification in run 14.

During several nitrations, separation was made more difficult by the presence of some white flocculent material which was observed in most instances to dissolve later in the acid phase. This material could not be conveniently handled and no analysis was made. Separations of the acid and product layer were generally quite clean without quenching. At temperatures of 0°C. and below, separation often took an hour, but separations at 10° and 20° took place rapidly, usually within 20 minutes.

C. Spent Acid Stabilization and Recovery

The spent acid from all the TEGDN reactions, as has been mentioned above, is relatively unstable, i. e. it begins to evolve heat and fume off at from a few minutes after nitration to a few hours, depending on the storage temperature and other conditions. It was found that on extraction with methylene chloride for recovery of any dissolved TEGDN the acid became somewhat more stable than an acid without extraction, but even an impractically large amount of solvent for extraction did not produce stabilization satisfactory for storage.

Spent acid to which an equal weight of 95% sulfuric acid was added became stable, at least for several days, at room temperature. The separated spent acid when placed in storage in an ice refrigerator at near 0°C. is stable to the extent that no visible decomposition takes place for up to 24 to 26 hours; however, we found that the nitric acid content falls off, showing a slow non-violent decomposition, which probably would eventually become stable.

To secure the maximum information with a minimum of time and expense, the study of spent acids was limited to the acids from the reaction of optimum yield, so nitration #42 was selected as typical for spent acid work for the

remainder of this program. It was also realized that an equipment set-up for actual recovery and separation of the acids would not be possible, so it was decided to work out a method of converting the acids to a stable condition so that existing industrial acid plant practice could be used for final separation and concentration of nitric and sulfuric acids.

A stabilization process was developed which resulted in a product which can be stored indefinitely at 60° to 80°F. or heated for removal of the nitric acid fraction in a recovery unit. Samples taken throughout the process were analyzed for nitric acid content so that a final accounting could be made for all the nitric acid, in order to approximate the amount available for recovery.

The final stabilization process was evolved from various experiments and observations as follows:

1. Untreated separated spent acid exposed to atmosphere in mild weather evolved heat and began to decompose in from 8 to 60 minutes.
2. Spent acid to which an equal weight of 95% sulfuric acid was added became stable to the extent that it could be heated to 90°C., without evidence of rapid decomposition, and would stand unchanged for at least several days.
3. Untreated spent acid stored at 0°C. was stable for 24-26 hours, possibly longer, although there was a slow non-violent decomposition with loss of nitric acid.
4. Spent acid with solvent extraction (up to 100% methylene chloride washed four times) was semi-stable for 24 hours; if the acid was agitated, it would begin to fume, then settle down when agitation ceased.

It was then seen that the acids remaining in the vessels which had been allowed to stand untreated (or unstabilized) after going through a spontaneous decomposition were now relatively stable, although the atmosphere in the area had been contaminated with acid and nitrogen oxide fumes, and considerable quantities of the acid were lost. For this reason and because the time and rate of decomposition should not be left to chance, a method was sought for controlling the time of starting of the decomposition and the rate or degree of violence, and to confine the gaseous products for recovery of acid and/or atmospheric pollution control.

5. A process similar to that being tried for Petrin spent acid was suggested by Mr. Maurice Baer of Picatinny Arsenal which, with modification and additions, became the final process.

Spent acid from refrigerated storage was placed in a reservoir and allowed to drip slowly into concentrated sulfuric acid at $+150^{\circ}\text{C}$. in a vessel on a hot plate. Vapors were to be forced out through a condenser to liquify any nitric acid which may be distilled from the hot acid mixture. The choice of acid temperature and rate of feed was not advantageous as vapors were evolved rather rapidly and a charred mass was formed in the acid vessel.

6. The same type of experiment was repeated with the sulfuric acid in a water bath equipped with an agitator and holding the acid at 65°C . The spent acid was fed in at a slower rate. There were no visible effects, no liquid acid was recovered in the condenser. The mixture of spent acid and sulfuric acid in the decomposition vessel was found to be approximately the same stability as was described in Item 2, above.

7. A similar experiment was repeated at an acid temperature of 90°C. with the same results as in Item 6, above.
8. Separated spent acid, removed from refrigerated storage, was placed in a flask fitted with a condenser and a receiver. This was allowed to warm up with no heat addition (other than from atmospheric temperature, 70°F. pickup). The acid temperature rose to 50°C. in about 30 minutes and then at 50°C. rose rapidly (i. e. in 4 to 5 seconds) to 75°C. Dark red fumes were evolved, no liquid was condensed, gas was not collected nor measured. There was a small (not measured) amount of acid dissolved in 50 ml of water which had been placed in the receiver. There was a measured overall weight loss of 10% of the charge. A nitrometer analysis showed a drop in the nitric acid concentration from 6.9% at start to 5.2% on residual. The acid remaining in the flask was found to be stable, i. e. several days observation indicated no further decomposition.
9. Another stabilization experiment was performed in the set-up shown in Figure 5. The cool (+5 - +10°C.) spent acid was allowed to drop at a controlled slow rate into the stabilizing flask which was held at a temperature of 75°C. The flask contained no H_2SO_4 . No increase in temperature was observed but dark red fumes were formed with each addition of spent acid. All gas evolved was conducted through a chilled condenser, a liquid trap and on into a gas collector by water displacement. After 30 minutes the red fumes disappeared from the gas and a transparent gas remained. By nitrometer analysis the spent acid was 6.9% HNO_3 before treatment and 5.4% HNO_3 after stabilization.

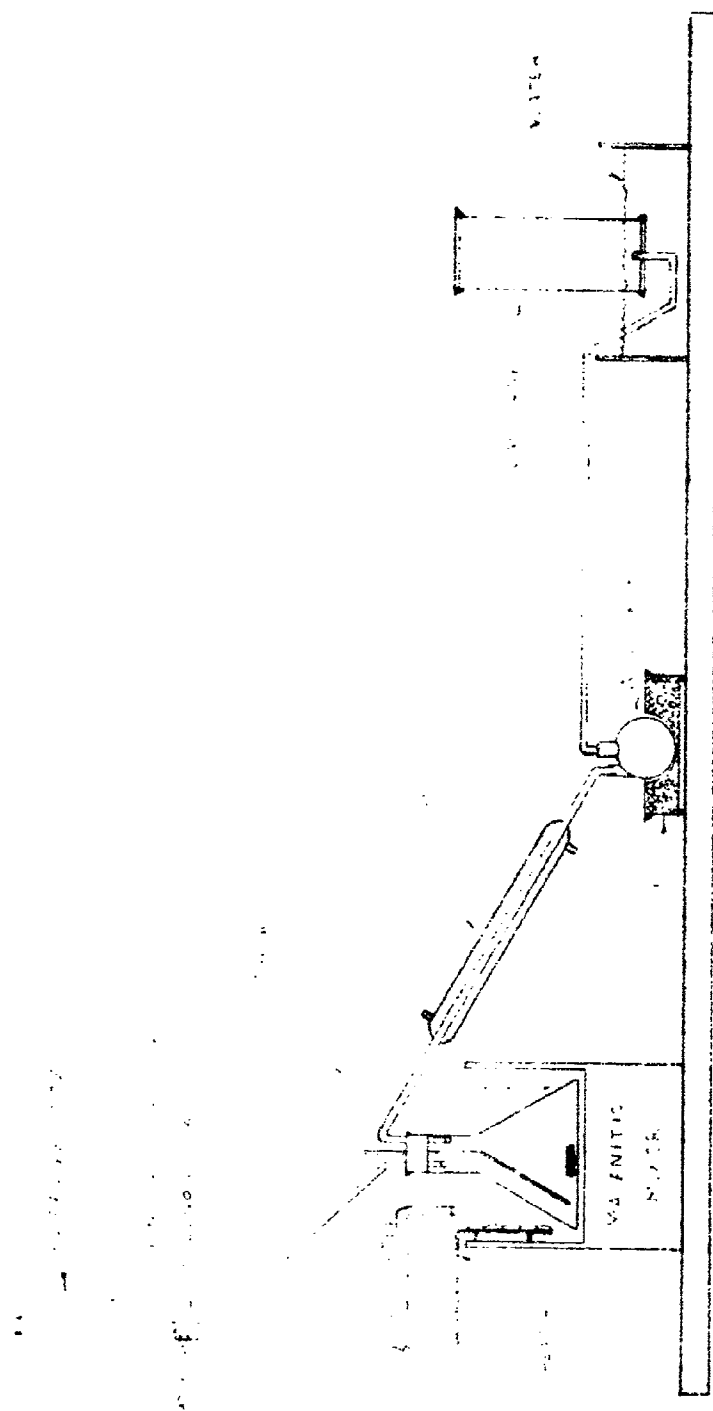
No liquid was condensed into the acid trap. As expected, the residual spent acid was stable on storage at room temperature.

10. Run #9 above was repeated with the decomposition flask held at 90°C. with essentially the same results. There was a difference in the nitric acid content, however. In Run #9 the spent acid had been held in 0°C. storage for about six hours after nitration completion before the start of the stabilization and had a nitric acid content of only 6.9%. For Run #10 the spent acid had been held in cold storage only about 2 hours before starting stabilization, and was found to have a nitric acid content of 20% before stabilization which dropped to 5.8% after stabilization. The final nitric acid concentrations being approximately the same as for Run #9, this leads us to believe that there was a slow decomposition during the cold storage period amounting to approximately 5% of nitric acid content in 6 hours at a temperature of 0° to 5°C.

No stabilized acid draw-off was provided in the system used as quantities were limited by the size of the reactor producing spent acid for this study. For larger batches or a continuous process a draw-off connection would be required. It would also be necessary to provide facilities to keep the spent acid chilled or otherwise stabilized before processing.

There was in stabilization Runs #9 and #10 an overall loss of 10% in weight, freshly separated spent acid to stabilized spent acid, approximated from measurements before and after stabilization and allowance for loss in storage before stabilization.

Financial and time factors prevented a thorough study on quantities and concentration of acids and gases in the spent acid. The following data should



SPENT ACID STABILIZATION ARRANGEMENT

FIGURE 6

be considered as representative only as they have not been confirmed by duplication after the apparatus had finally been adjusted for good operation and control. Other temperatures of decomposition and condensation should be tried at various rates of feed, etc.

To present an overall understanding of the spent acid stabilization and recovery, Table II based on nitration Run #42 and stabilization Runs #9 and #10 was prepared. It was assumed that in these processes no sulfuric acid was consumed.

The apparatus shown in Figure 5 provided some qualitative information about the gas from the stabilization procedure. In operation, the gas collected was red brown but on standing overnight became clear. Although some of the gas dissolved in the water associated with the collector, 82 ml remained undissolved from the stabilization of the 66.6 gm charge. The water in the collector showed a pH of 6.5 and practically no carbon dioxide in the gas phase in the collector. We believe that the water insoluble gases from stabilization might acceptably be released to the atmosphere from a reasonably tall stack. If 101 gm TEGDN has associated with it 82 ml of gas, then a plant producing 10,000 lbs. TEGDN per day would release only about 1320 cu. ft. of gas per day.

Since it was impossible (time and funds) to do any additional work on experimental acid recovery, we can only theorize on the stabilization and recovery of spent acid.

The 43.5% of nitric acid charge found associated with the product can largely be recovered from the wash water and concentrated to 68% by ordinary distillation. If it is desired to concentrate to greater extent, this can be done

TABLE II
Material Balance on Run No. 42

<u>Reactor Input</u>		<u>Reactor Output</u>	
HNO ₃	131.3 gm	Product Layer	HNO ₃ 57.1 gm
H ₂ SO ₄	51.6 gm		H ₂ SO ₄ 6.8 gm
H ₂ O	4.3 gm		H ₂ O 18.1 gm
TEG	<u>75.0 gm</u>		TEGDN 101.0 gm
Total	262.2 gm	Acid Layer	HNO ₃ 13.0 gm
			H ₂ SO ₄ 32.7 gm
			Other 20.3 gm
		Loss to Atmosphere	<u>12.6 gm</u>
		Total	262.2 gm
<u>Nitric Acid Flow</u>			
Consumed in producing 101.0 gm TEGDN		% Original HNO ₃	
Found in product layer		53.0 gm	40.3
Found in stabilized spent acid		57.1 gm	43.5
Loss to atmosphere in reaction & stabilization		3.5 gm	2.7
		<u>17.7 gm</u>	<u>13.5</u>
		131.3 gm	100.0

by existing methods now in regular operation for manufacture of concentrated nitric acid. The cost of the water evaporation in this recovery must be balanced against the cost of new acid and/or the availability of satisfactory spent acid disposal methods. Most certainly some of the nitric acid will eventually be neutralized by the final soda wash of the nitrated product. Disposal of this nitrate salt is not expected to cause any unsurmountable problem.

The 2.7% of total nitric acid charge which is in the stabilized spent acid can be recovered by conventional techniques.

The data of Table III on spent acid stability versus water content is plotted in Figure 6.

D. Yield Study

Using the procedure described earlier, fifty-three (53) runs were made under various conditions: (1) temperatures of -15° , 0° , 10° and 20°C . (2) glycol to mixed acid ratios of 0.5 through 0.33; (3) with no solvent and with methylene chloride as solvent, (4) with sulfuric acid as the hydrophilic agent and with acetic anhydride as the hydrophilic agent; (5) glycol addition times from 6 to 70 minutes. Table IV summarizes the data collected on these runs.

Figure 7 shows the compositions of the mixed acids on a triangular graph for all runs made.

Table V shows the runs made at various temperatures and ratios of mixed acid to glycol.

Table VI provides a comparison of the yields obtained at three temperatures and a mixed acid ratio of 2.5. It appears that 10°C . provides the highest average yield.

SPENT ACID STABILITY VS WATER CONTENT

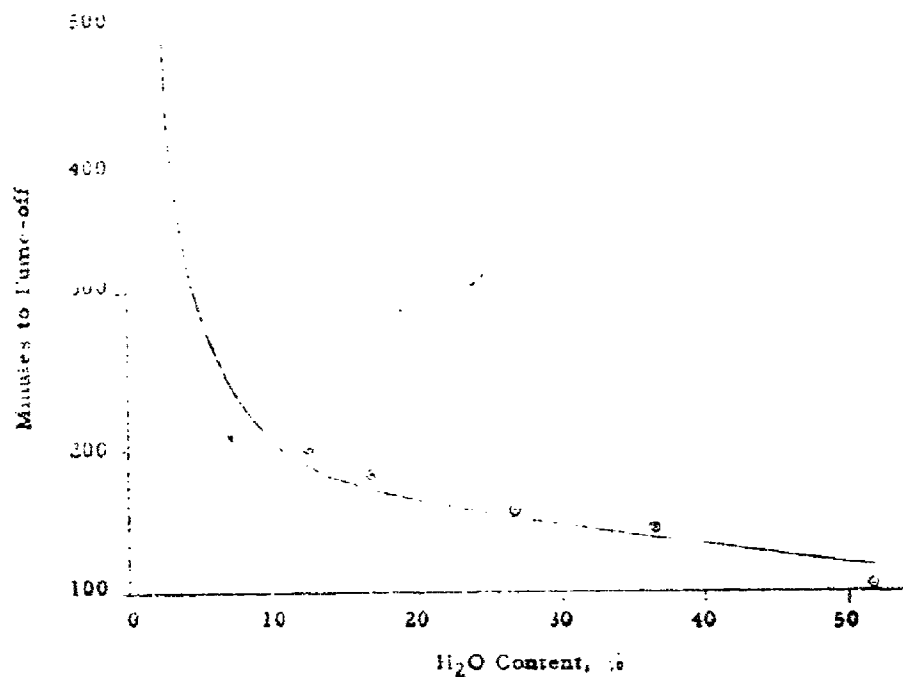


TABLE III. Spent Acid Stability Versus Water Content

Sample Number	Acid Analysis				Minutes to Fume-off
	TEGDN	HNO ₃	H ₂ SO ₄	H ₂ O	
1	1.0	68.5	28.2	2.3	Stable to 4 days
2	1.0	65.1	26.7	7.2	210 min
3	1.0	61.6	25.3	12.1	200 min
4	1.0	58.2	23.9	16.9	180 min
5	1.0	51.2	21.1	26.7	155 min
6	1.0	44.4	18.1	36.5	145 min
7	1.0	33.9	13.8	51.3	105 min

Table VII presents the effect of mixed acid to glycol ratios on yields at 10°C. and indicates that a ratio of 2.5 or 3.0 is superior to 2.0.

Table VIII illustrates data on the yield as effected by the nitric acid to glycol mole ratio. It appears, with a few exceptions, that the high ratios of nitric acid to glycol gave the higher yield.

Figures 8, 9 and 10 present additional data in the form of yield isopleths.

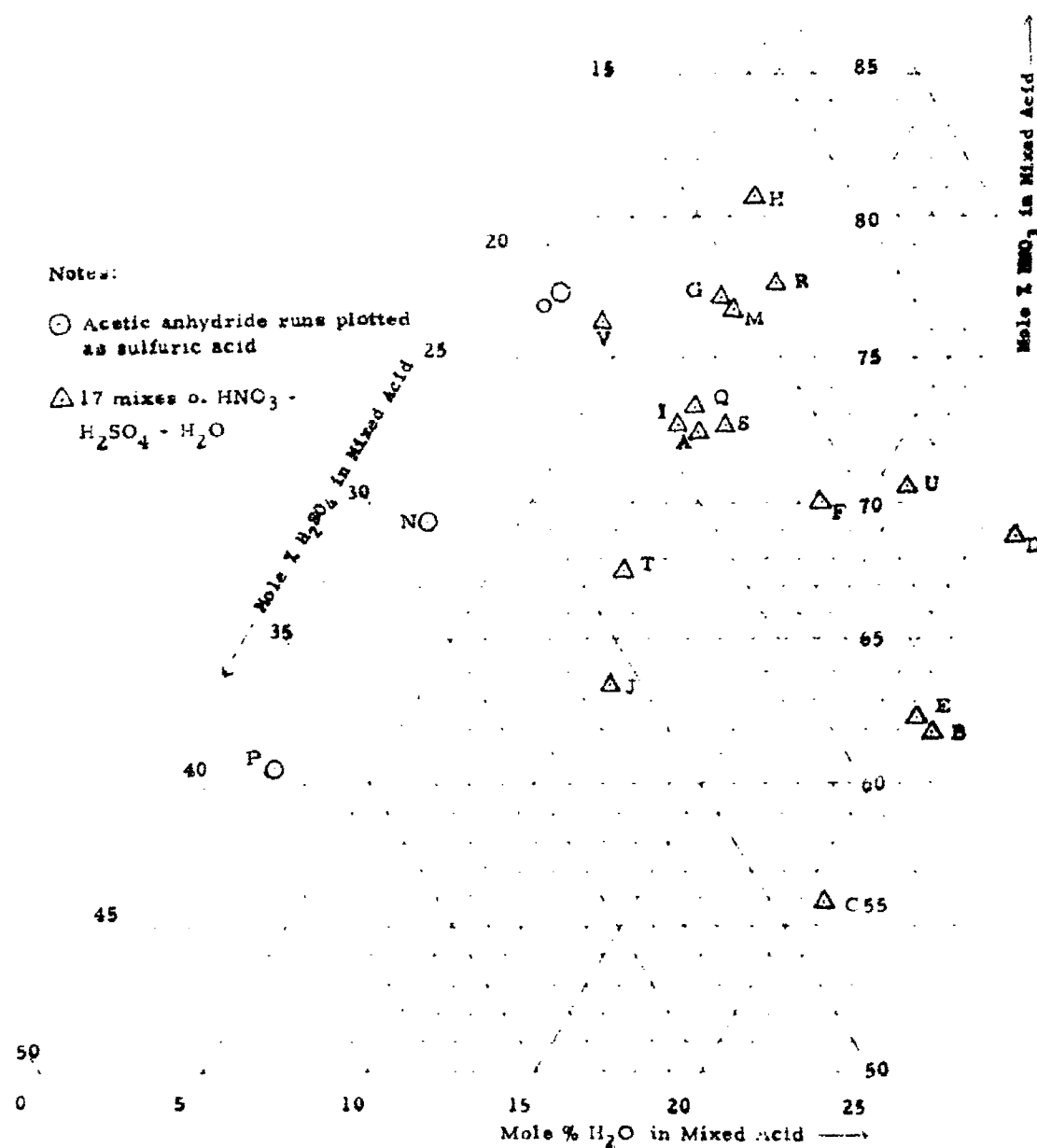


FIGURE 7. Three Component Plot of All Acid Mixes for all Runs Made.

NOTES

1. ** Products from all nitration runs have assay between 98% and 102% except runs marked ** as follows: Assay Method in accord with MIL-Std-286 28 June 1956 Method 208.1.2 (T)

Run No. 5 - 97.5% Assay as TEGDM
7 - 96.5
8 - 97.0
14 - 96.5
22 - 96.2

2. (*) Acetic anhydride $(CH_3CO)_2O$ mol. wt. 102.1, used in place of H_2SO_4 for nitration runs 37, 38 and 39 although shown in the sulfuric acid columns 4, 8 and 11.
3. (+) Methylene chloride, (M.C.) used in reaction runs 46, 47, 48 by addition to reactor prior to adding glycol.
4. (φ) Yields shown are those obtained without extraction of spent acid, gain in yield due acid extraction shown each run where extraction was made.

Column Explanation

- | | |
|----------|---|
| 1 | Nitration run numbers |
| 2 to 5 | Inclusive are total wt. in grams of materials in reaction system calculated to a 100% strength material, excluding any methylene chloride |
| 6 to 9 | Inclusive all materials in reaction system calculated to mole % basis of M.A. |
| 10 to 12 | Inclusive acids and water in reaction system on a mole % basis |
| 13 | Ratio total mixed acid to glycol, weight basis |
| 14 | Ratio total HNO_3 to glycol on weight basis |
| 15 | Ratio total HNO_3 to glycol on mole/mole basis |
| 17 | Reaction time to add glycol |
| 18 | Holding time for reaction with agitation, not incl. time for separation of product from acid |
| 19 | Yield in % based on TEG |
| 20. | Mixture letter designation |
| 21. | Nitration run numbers |



TABLE IV. Cumulative Nitration Data

1	2	3	4	5	6	7	8	9	10	11	12
Run No.	Grams TEG	in Reaction System			Mole % in Reaction System				Mole % in Mixed Acid		
		HNO ₃	H ₂ SO ₄	H ₂ O	TEG	HNO ₃	H ₂ SO ₄	H ₂ O	HNO ₃	H ₂ SO ₄	H ₂ O
1	100.0	173.2	70.8	6.0	14.9	61.5	16.1	7.5	72.3	18.9	8.8
2	100.0	173.2	70.8	6.0	14.9	61.5	16.1	7.5	72.3	18.9	8.8
3	100.0	173.2	70.8	6.0	14.9	61.5	16.1	7.5	72.3	18.9	8.8
4	100.0	173.2	70.8	6.0	14.9	61.5	16.1	7.5	72.3	18.9	8.8
5**	100.0	163.5	70.8	15.8	13.7	53.4	14.8	18.1	61.9	17.1	21.0
6	100.0	140.4	94.4	15.2	14.5	46.3	20.9	18.3	55.8	23.6	20.6
7**	100.0	187.0	47.2	15.8	13.4	59.4	9.6	17.6	68.6	11.1	20.3
8**	75.0	121.0	52.5	11.5	13.9	53.4	14.9	17.8	62.1	17.3	20.6
9	75.0	130.7	46.9	7.4	15.1	59.9	13.8	11.9	70.0	16.1	13.9
10	75.0	148.8	47.2	4.0	14.0	66.3	13.5	6.2	77.1	15.7	7.2
11	75.0	148.6	35.3	3.5	14.7	69.2	10.6	5.5	80.9	12.4	6.7
12	75.0	130.0	53.1	4.2	15.0	61.8	16.2	7.0	72.7	19.1	8.2
13	75.0	111.4	70.9	5.2	15.2	54.0	22.0	8.8	63.7	25.9	10.4
14**	75.0	148.6	35.3	3.5	14.7	69.2	13.5	5.5	80.9	12.4	6.7
15	75.0	148.6	35.3	3.5	14.7	69.2	13.5	5.5	80.9	12.4	6.7
16	75.0	148.6	35.3	3.5	14.7	69.2	13.5	5.5	80.9	12.4	6.7
17	75.0	148.6	35.3	3.5	14.7	69.2	13.5	5.5	80.9	12.4	6.7
18	75.0	148.6	35.3	3.5	14.7	69.2	13.5	5.5	80.9	12.4	6.7
19	75.0	148.6	35.3	3.5	14.7	69.2	13.5	5.5	80.9	12.4	6.7
20	75.0	148.6	35.3	3.5	14.7	69.2	13.5	5.5	80.9	12.4	6.7
21	75.0	148.6	35.3	3.5	14.7	69.2	13.5	5.5	80.9	12.4	6.7
22**	75.0	148.6	35.3	3.5	14.7	69.2	13.5	5.5	80.9	12.4	6.7
23	100.0	178.0	72.5	5.9	14.1	62.3	16.1	7.2	72.7	18.8	8.4
24	100.0	173.4	70.8	5.8	14.9	61.6	16.1	7.2	72.4	19.1	8.4
25	100.0	173.4	70.8	5.8	14.9	61.6	16.1	7.2	72.4	19.1	8.4
26	100.0	148.6	94.5	6.9	15.2	53.9	22.1	8.8	63.6	26.0	10.4
27	100.0	198.2	47.2	4.6	14.6	67.2	10.6	5.6	81.0	12.4	6.6
28	75.0	148.6	47.2	4.2	14.0	66.0	13.5	6.5	76.7	15.7	7.6
29	75.0	130.0	53.1	4.2	15.0	61.8	16.2	7.0	72.7	19.1	8.2
30	75.0	111.4	70.8	5.1	15.2	53.9	22.2	8.6	63.8	26.0	10.2
31	83.4	173.4	70.8	5.7	12.8	63.3	16.6	7.3	72.4	19.1	8.4
32	83.4	148.6	94.5	6.9	13.0	55.4	22.6	9.0	63.7	26.0	10.3
33	83.4	198.2	47.2	4.6	12.5	70.8	10.9	5.8	81.0	12.4	6.6
34	66.8	148.6	47.2	4.2	12.7	67.0	13.7	6.6	76.7	15.7	7.6
35	62.5	130.0	53.1	4.2	12.8	63.4	16.7	7.2	72.7	19.1	8.2
36	62.5	111.4	70.8	5.1	13.0	55.5	22.6	8.9	63.8	26.0	10.2
37*	62.5	111.5	75.0*	1.0	14.0	59.4	24.7*	1.8	69.2	28.7*	2.1
38*	62.5	130.0	56.2*	1.1	13.5	66.8	17.8*	2.0	77.1	20.6*	2.3
39*	66.8	99.1	100.0*	0.9	14.6	51.6	32.2*	1.6	60.5	37.6*	1.9
40	100.0	158.5	37.8	3.7	17.7	66.7	10.2	5.4	81.0	12.4	6.6
41	100.0	138.7	56.7	4.6	18.0	59.5	15.6	6.9	72.5	19.1	8.4
42	75.0	131.3	51.6	4.3	14.9	62.2	15.8	7.1	73.2	18.5	8.3
43	75.0	131.3	51.6	4.3	14.9	62.2	15.8	7.1	73.2	18.5	8.3
44	75.0	131.3	51.6	4.3	14.9	62.2	15.8	7.1	73.2	18.5	8.3
45	75.0	131.3	51.6	4.3	14.9	62.2	15.8	7.1	73.2	18.5	8.3
46+	75.0	131.3	51.6	4.3	14.9	62.2	15.8	7.1	73.2	18.5	8.3
47+	75.0	131.3	51.6	4.3	14.9	62.2	15.8	7.1	73.2	18.5	8.3
48+	75.0	131.3	51.6	4.3	14.9	62.2	15.8	7.1	73.2	18.5	8.3
49	100.0	190.8	53.3	5.9	14.6	66.3	11.9	7.2	77.7	13.5	8.8
50	100.0	175.6	67.5	6.6	14.8	61.9	15.3	8.1	72.6	17.5	10.0
51	75.0	119.0	64.2	4.3	15.2	57.3	19.9	7.6	67.6	23.5	8.9
52	82.6	142.7	42.2	9.5	14.6	60.5	11.4	13.9	70.3	13.5	16.2
53	76.3	131.8	53.6	2.0	13.6	64.2	16.8	3.4	75.1	19.5	6.4

2

12	13	14	15	16	17	18	19
Acid H ₂ O	Ratio Acid to Glycol By wt	wt. HNO ₃	Moles HNO ₃	Reaction Temp. °C.	Reaction Times Minutes Add'n	Hold	Yield %
8.8	2.5	1.73	4.1	0	22.5	15	33.0
8.8	2.5	1.73	4.1	0	14.0	70	63.8
8.8	2.5	1.73	4.1	-15	70.0	40	51.7
8.8	2.5	1.73	4.1	10	13.5	40	54.2
21.0	2.5	1.62	3.9	0	39	30	55.8
20.6	2.5	1.40	3.3	0	21	45	58.4
20.3	2.5	1.9	4.5	0	16	49	30.2
20.6	2.5	1.6	3.8	10	9	40	55.9
13.9	2.65	1.7	4.0	10	8	2	56.0
7.2	2.5	2.0	4.8	0	15	45	77.6
6.7	2.5	2.0	4.8	0	15	45	83.0
8.2	2.5	1.7	4.0	0	15	45	82.0
10.4	2.5	1.5	3.6	0	15	45	68.7
6.7	2.5	2.0	4.8	10	14	45	76.4
6.7	2.5	2.0	4.8	18	15	45	75.6
6.7	2.5	2.0	4.8	0	23	37	68.0
6.7	2.5	2.0	4.8	0	15	45	72.6
6.7	2.5	2.0	4.8	0	18	30	79.1
6.7	2.5	2.0	4.8	0	12.5	40	75.0
6.7	2.5	2.0	4.8	20	9.5	17	72.2
6.7	2.5	2.0	4.8	18	6	-	-
6.7	2.5	2.0	4.8	18	6	3	70.5
8.4	2.5	1.8	4.3	10	14	4	81.8
8.4	2.5	1.7	4.0	10	13	3	79.7
8.4	2.5	1.7	4.0	10	13	3	-
10.4	2.5	1.5	3.6	10	15	3	71.7
6.6	2.5	2.0	4.8	10	13	3	79.6
7.6	2.5	2.0	4.8	10	12	3	81.4
8.2	2.5	1.7	4.0	10	12	3	80.9
10.2	2.5	1.5	3.6	10	11	3	75.8
8.4	3.0	2.1	5.0	10	14	4	80.2
10.3	3.0	1.8	4.2	10	13.5	3	73.7
6.6	3.0	2.4	5.7	10	12.0	5	78.2
7.6	3.0	2.2	5.2	10	11.0	5	79.2
8.2	3.0	2.1	5.0	10	10.5	3	78.6
10.2	3.0	1.8	4.3	10	10.0	3	71.1
2.1	3.0	1.8	4.3	10	9.0	3	32.5
2.3	3.0	2.1	5.0	10	9	4	4.0
1.9	3.0	1.5	3.6	10	10	5	49.9
6.6	2.0	1.6	3.8	10	10.5	2	47.7
8.4	2.0	1.4	3.3	10	12	3	59.1
8.3	2.5	1.8	4.3	10	10	3	80.2
8.3	2.5	1.8	4.3	10	11	3	78.0
8.3	2.5	1.8	4.3	10	10	3	80.0
8.3	2.5	1.8	4.3	10	11.5	5	81.0
8.3	2.5	1.8	4.3	10	7	4	76.3
8.3	2.5	1.8	4.3	10	9.5	5	79.2
8.3	2.5	1.8	4.3	10	7	3	80.0
8.4	2.5	1.9	4.5	10	15	4	75.6
9.5	2.5	1.8	4.3	10	10.5	6	80.0
9.0	2.5	1.6	3.8	10	10	3	73.9
16.4	2.35	1.7	4.0	10	10	3	60.6
4.0	2.46	1.7	4.0	10	9	4	73.8

18	19	20	21	
in Times				
ates	Yield	Mix	Mun	
Hold	%	Letter	No.	Remarks - Special Comments
15	33.0	A	1	6 samples @ 5 min for speed of reaction
70	63.8	A	2	12 " " 5 " " " " "
40	51.7	A	3	12 " " 3 " " " " " (Acid silica gel)
40	54.2	A	4	12 " " 3 " " " " "
30	55.8	B	5	Low assay 97.5%
45	58.4	C	6	
49	30.2	D	7	H ₂ O quenched Due no separation at 60 mm
40	55.9	E	8	Aubertin Method - 20% H ₂ SO ₄ for product recovery wash
2	56.0	F	9	Ditto - used 65% oleum to reduce H ₂ O
45	77.6	G	10	H ₂ O quench due plugged separator drain
45	83.0	H	11	
45	82.0	I	12	
45	68.7	J	13	
45	76.4	H	14	Low assay 96.5%
45	76.6	H	15	Fuming during reaction - good separation
37	68.0	H	16	
45	72.6	H	17	
30	79.1	H	18	
40	75.0	H	19	
17	72.2	H	20	
-	-	H	21	10% Silica Gel in reactor - no separation - no yield data
3	70.5	H	22	10% Drierite " " (96.2% assay)
4	81.8	A	23	
3	79.7	I	24	
3	-	I	25	Yield data lost
3	71.7	J	26	
3	79.6	H	27	
3	81.4	M	28	
3	80.9	I	29	
3	75.8	J	30	
4	80.7	I	31	
3	73.7	J	32	
5	78.2	H	33	Fuming during last half nitration
5	79.2	M	34	
3	78.6	I	35	
3	71.1	J	36	
2	32.5	N	37	Note 2* Fumed during first half reaction
4	4.0	O	38	Note 2*
5	48.9	P	39	Note 2* Fumed during first half reaction
2	47.7	H	40	No separation - quenched in H ₂ O
3	59.1	I	41	Fuming during reaction and separation - quenched
3	80.2	Q	42	M.C. ext. of spent acid improves yield by 1.81%
3	78.0	Q	43	Spent acid stabilized for 24 hrs. by adding 50% wt. H ₂ SO ₄
3	80.0	Q	44	M.C. ext. S.A. improves yield by 1.21%
5	81.0	Q	45	" " " " " " 1.61%
4	76.3	Q	46	10% M.C. added to reactor
5	79.2	Q	47	30% M.C. " " " Yield gain .7% Acid Ext. #
3	80.0	Q	48	10% M.C. " " " " " .6% " " #
4	79.6	R	49	M.C. ext. Spent acid improves yield by .41%
6	80.0	S	50	" " " " " " .41%
3	73.9	T	51	" " " " " " .71%
3	60.6	U	52	
4	73.8	V	53	

4

TABLE V

Number of Runs Made At Various Temperatures and Ratios
of Mixed Acid to Glycol

Mix	0°C.		10°C.		20°C.	
	Run	Ratio	Run	Ratio	Run	Ratio
A	1, 2	2.5	4, 23	2.5		
B	5	2.5				
C	6	2.5				
D	7	2.5				
E			8	2.5		
F			9	2.65		
G	10	2.5				
H	11, 16, 17, 18, 19	2.5	14, 27, 33*, 40**	2.5	15, 20, 21, 22	2.5
I	12	2.5	24, 29, 31*, 35* 41**, 25	2.5		
J	13	2.5	26, 30, 32*, 36*	2.5		
M			28, 34*	2.5		
Q			42, 43, 44, 45, 46	2.5		
R			49			
S			50			
T			51			
U			52			
V			53			

* Ratio 3.0

** Ratio 2.0

TABLE VI

Effect of Temperature On Yield At Mixed Acid to Glycol
Ratio of 2.5

<u>Temperature</u>	<u>M. &</u>	<u>Run No.</u>	<u>Yield</u>	
0°C.	H	11	83.0%	
0°C.	H	16	68.0%	Max 83.0%
0°C.	H	17	72.0%	Ave 75.4%
0°C.	H	18	79.1%	Min 68%
0°C.	H	19	75.0%	
10°C.	H	14	76.4%	Max 79.6%
10°C.	H	27	79.6%	Ave 76.0%
				Min 76.4%
20°C.	H	15	76.6%	
20°C.	H	20	72.2%	Max 76.6%
20°C.	H	21	-	Ave 73.1%
20°C.	H	22	70.5%	Min 70.5%

TABLE VII

Effect of Mixed Acid to Glycol Weight Ratio on Yield
at 10°C.

<u>Ratio Mixed Acid to Glycol</u>	<u>Average Yield</u>	<u>Mix</u>	<u>Run Number</u>
2.0	59.1	I	41
2.5	80.5	I	24 & 29
3.0	79.1	I	31 & 35
2.0	47.7	II	40
2.5	78.0	II	14 & 27
3.0	78.2	II	33
2.0	73.7	J	26 & 27
3.0	72.7	J	32 & 36
2.5	81.4	M	28
3.0	79.2	M	34

TABLE VIII

Yield Data For Various Nitric Acid to Glycol
Mole Ratios

<u>Mole Ratio</u> <u>Nitric Acid</u> <u>Glycol</u>	<u>Yield</u>	<u>Mix</u>	<u>Run</u>
4.6	85	H	11
4.0	82	I	12
4.3	81.6	A	23
4.8	81.4	M	28
4.	80.9	I	29
5.0	80.2	I	31
4.3	80.2	Q	42
4.3	80.0	Q	44
4.3	81.0	Q	45
4.3	80.0	Q	48
4.3	80.0	S	50
4.8	77.6	G	10
4.8	76.4	H	14
4.8	76.6	15	
4.8	75.0	H	19
3.6	75.8	J	30
4.2	73.7	J	32
4.3	76.3	Q	46
3.8	73.9	T	51
4.0	73.8	V	53
4.1	33	A	2
4.1	52	A	3
4.1	54	A	4
4.1	56	B	5
3.3	58	C	6
4.5	30	D	7
3.8	56	E	8
4.0	56	F	9
4.8	68	H	16
3.8	48	H	40
3.3	59	I	41
4.3	61	U	52

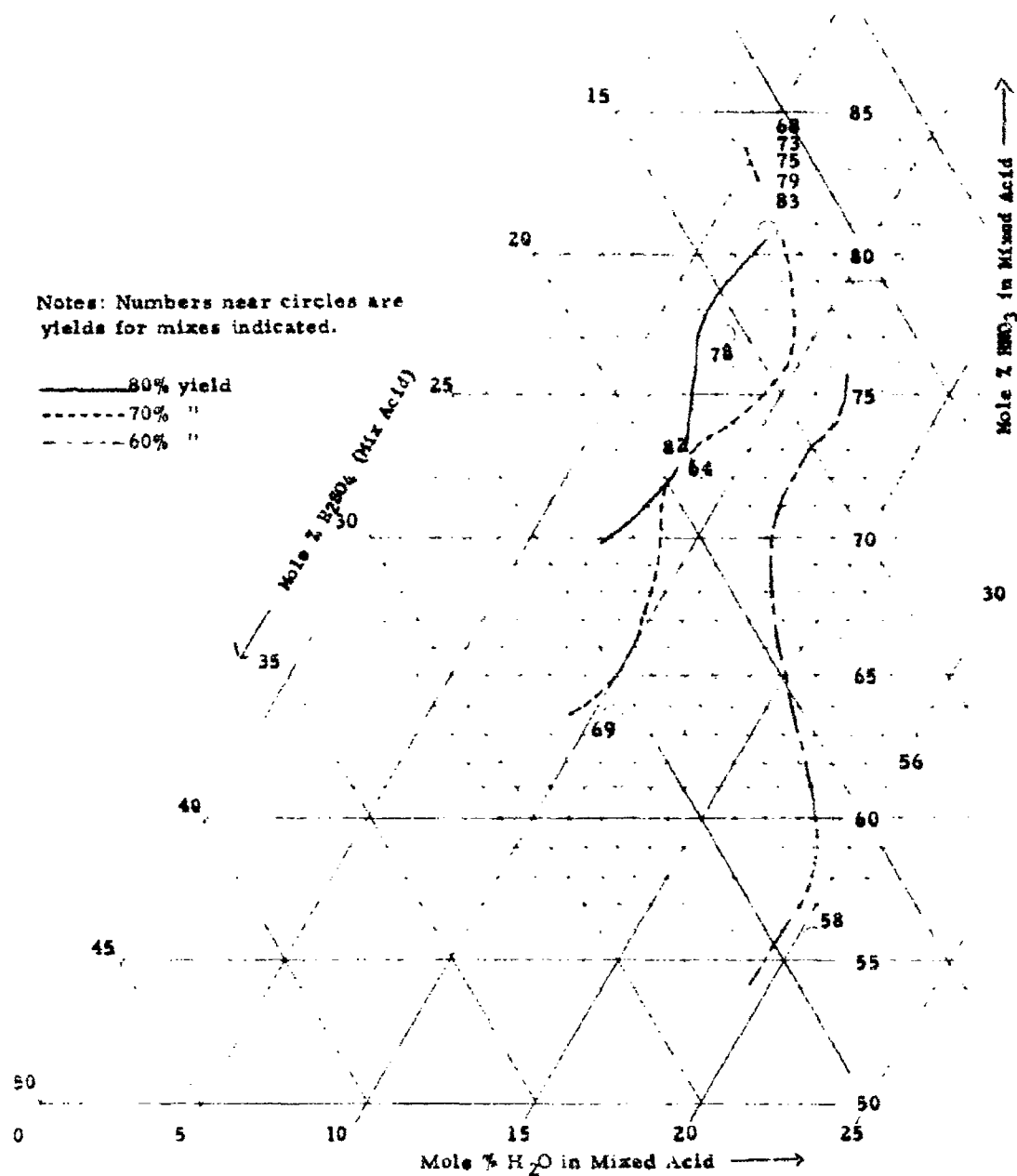


FIGURE 8. Yield isoplethes for Reaction at 0°C. and Mixed Acid to Glycol Ratio of 2.5

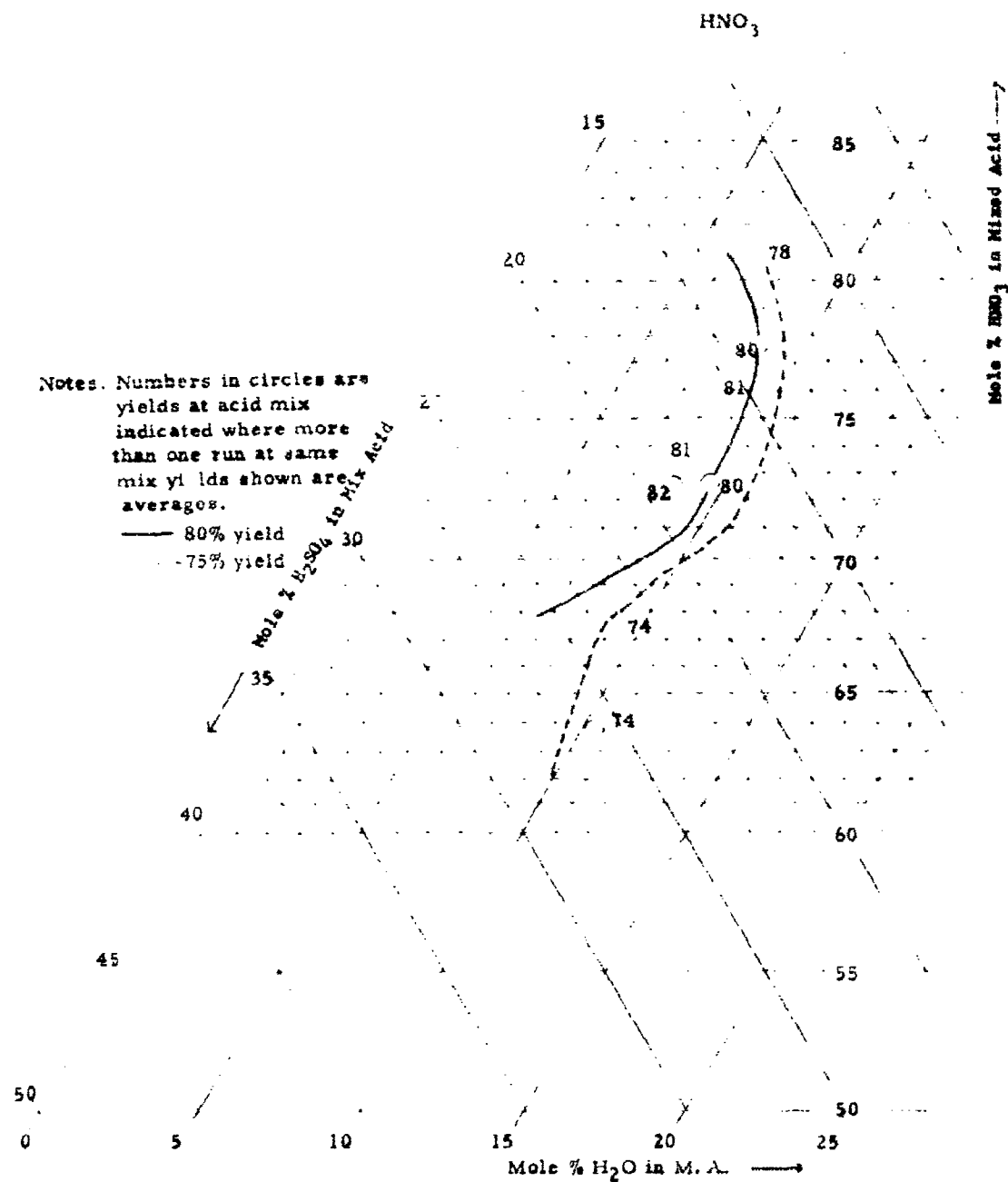


FIGURE 7. Yield Isoplethes for Reaction at 10°C. and Mixed Acid to Glycol Ratio of 2.5

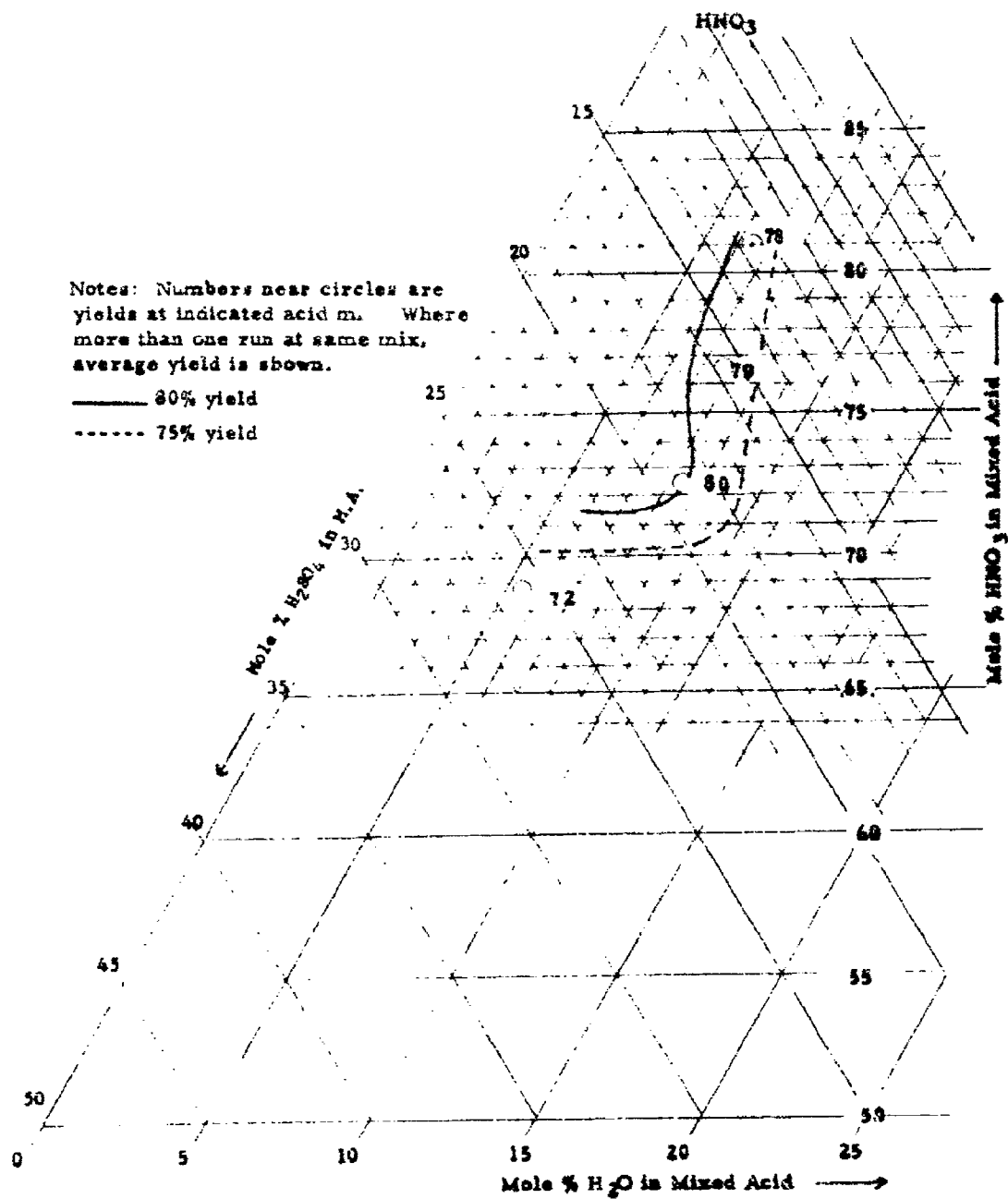


FIGURE 10. Yield Isopleths for Reaction at 10°C. and Mixed Acid to Glycol Ratio of 3:0

V. PRODUCTION COST STUDY

Due to the time required by the earlier phases of this study, very little time was available for a production cost study. Only a few qualitative remarks will be made.

With respect to analytical and control standards for raw materials, the specifications we have worked out for production appear satisfactory. We use Technical Grade TEG supplied by Jefferson Chemical Company. The nitric acid used is Technical Grade 98-99% and the sulfuric acid is Technical Grade 66°Be.

In-process control is primarily manual control of rate of feed using thermocouple indications. We quench the reaction mass thirty minutes or less after last addition of TEG. We do not recover the acids but we do recover the solvent. If we recovered the acids, we would not quench.

Study of the yield isopleth data presented indicates that the nitric acid concentration can vary from 70 to 80 mole per cent and give yields of the order of 80+%. In practice we are able to achieve 90+% with quenching. Since the cost of nitric acid is 1.5 times the cost of sulfuric acid, it is clear that the mixed acid with lower percentage of nitric acid would be the most economical for operation. It appears that the total reaction time (reaction + holding time) can be markedly reduced in order to increase the through-put and thus lower the total capital investment. Greater refrigeration capacity in our equipment would have permitted us to establish this experimentally.

A very important consideration in production costs is recovery of spent acids. It has been shown that the spent acids should be stabilized almost

immediately or kept refrigerated. They decompose within an hour at normal temperature. Our study showed that the addition of sulfuric acid would stabilize the spent acid but more work should be done to prove this is the most practical process on large scale operations.

VI. SUMMARY

1. There appears to be very little substantial literature on the nitration of triethyleneglycol. That of Aubertein appears most pertinent but a few other references were noted.
2. The chemical kinetics of the nitration of TEG is far from established. The experimental work done indicates that with some refinement of technique the rate of the reaction could be measured.
3. Yield data can best be presented by means of isopleths on a triangular diagram with nitric and sulfuric acid and water as the variables. The data obtained indicates and narrows the region of greatest promise but additional similar type data would permit more precise selection of the optimum conditions. All information and experience considered good operating procedure for preparing TEGDN would involve the following conditions:

- 1) Temperature of nitration : 10°C.
- 2) Composition mixed acid : 73 mol % HNO_3 , 19 mol % H_2SO_4
8 mol % H_2O
- 3) TEG/mixed acid : 1/2.5 by weight
- 4) Rate of addition of TEG with : Rapidly as heat exchange permits
agitation

and should provide a yield of 80% or better without quenching. Our production experience has shown that with quenching and use of methylene chloride as a solvent, yields up to 95% may be obtained.

4. Spent acid from nitrations presents several significant problems:
 - 1) disposal without pollution of atmosphere or streams
 - 2) possible fume-off or detonation during storage
 - 3) economic recovery of component acids.

The work done indicates that safe stabilization of the spent acid can be achieved by the addition of sulfuric acid. Nitric acid can then be separated from the stabilized spent acid by conventional methods but the low concentration of nitric acid we found in the stabilized spent acid complicates the problem.

Stabilization of spent acid without the addition of sulfuric acid may be accomplished if it can be processed immediately by the controlled decomposition as described in Section V c of the report.

Since about 43% of the HNO_3 used is found in the product layer, an efficient water extraction procedure is indicated to economically recover nitric acid.

VII RECOMMENDATIONS

Due to the fact that large quantities of TEGDN may be used in the nation's solid propellant program in the future and that the subject contract was not significant enough in funds to be as comprehensive as desirable, it is recommended that the study of TEG nitration be extended to carry out a more comprehensive study of the factors investigated in this report and to increase the scale of investigation to say ten pound quantities for a better engineering evaluation.

	Page
A. References	47, 48
B. Heat of Reaction for Nitration of TEG	49, 50
C. Densities of Mixed Acids	51
D. Vapor-Liquid Equilibrium for Aqueous Nitric Acid	52
E. Relative Activity Coefficients of Mixed Acids	53
F. Definition of Symbols	54

APPENDIX "A"

References

- a. "Properties of Explosives of Military Interest" by W. R. Tomlinson, Jr., revised by O. E. Sheffield - Picatinny Arsenal Technical Report No. 1740, Revision 1, dated April 1958.
- b. Research Department publications, Propellux Chemical Division, Chromalloy Corporation.
- c. "Viscosities and Indices of Refraction of Various Liquid Nitrate Esters" by Jacques Bolleau and Maurice Thomas - Memorial des poudres et salpêtres (Paris), 33, 155-7 (1951).
- d. "Preparation and Properties of Several Glycol Nitrates" by P. Aubertein - Mem. poudres, 30, 7-42 (1948) (Chem. Abstracts 43, 3531).
- e. "Apparatus for the Measurement of Vapor Pressure and Ignition or Decomposition Temperature at Pressures above Atmospheric" by A. Greenville Whittaker (U.S. Nav. Ord. Test Station) - Review of Scientific Instruments, 28, 360-4, (1957).
- f. "Thermochemical Data Relative to the Constituents of Propellants" by P. Javernier - Mem. poudres, 38, 301-36 (1956) (Chem. Abstracts 1957, 15952 e).
- g. "Surface Temperature of Burning Liquid Nitrate Esters" by R. Steinberger and K. E. Corder - J. Phys. Chem., 59, 255-7 (1955).
- h. "Analysis of Propellants by Infrared Spectroscopy" by F. Pistara, Analytical Chemistry, 25, 844-56 (1953).
- i. "Shock Sensitivities of Liquid Nitrate Esters" by L. Medard, Mem. poudres, 31, 131-43 (1949).
- j. Liebig's Annalen der Chemie (3), 67, 275 (1863) - per a. above
- k. " " " (3), 69, 331, 351 (1863) - per a. above
- l. Private Communication, M. Baer, Picatinny Arsenal to T. N. Scortia, Propellux Chemical Division
- m. Navord Report 43-45 German Powder Development 15 Sept 1945
Translation of Uto Galiwitz's "Die Geschützladung" by R. A. Gabley, J. Wasser and K. Mielow
- n. Private Communication, D. Kite, Picatinny Arsenal to D. R. Deal, Propellux Chemical Division

APPENDIX "A"

- c. W. R. Lewis and T. J. Such, Ind. Chem., **32**, 1095 (1946)
- d. C. McKinley and R. R. White, Trans. Am. Inst. Chem. Engrs.,
40, 143 (1944)
- e. Private communication, D. Kite - Picatinny Arsenal - to D. R. Deal - Propellor Chemical Division.
Impact sensitivity N.G. 1" with 1 lb. wt.
 " " TEGDN 2" " 4.4 lb. wt.

APPENDIX "B"

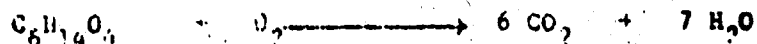
HEAT OF REACTION FOR NITRATION OF TEG

1. Heat of Formation, Triethylene Glycol:

a. Heat of Combustion, TEG, (PCL Calorimetric Measurement):

$$\begin{aligned} H_c &= -3.37 \text{ kg-cal/gram} \\ &= (-3.37)(150.17) = -851.2 \text{ kg-cal/gm-mole} \end{aligned}$$

b. Combustion of TEG:



c. Heats of Formation:

$$(1) H_f, \text{CO}_2 (g) = -94.40 \text{ kg-cal/gm-mole (Physical Chemistry-MacDougall)}$$

$$(2) H_f, \text{H}_2\text{O} (l) = -68.36 \text{ kg-cal/gm-mole (" ")}$$

$$(3) H_f, \text{TEG} (l) = 6(-94.40) + 7(-68.36) - (-851.2)$$

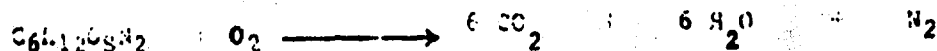
$$H_f, \text{triethylene glycol} (l) = -193.7$$

2. Heat of Formation, Triethylene Glycol Dinitrate:

a. Heat of Combustion, TEGDN (Picatinny Arsenal Tech. Rept. 1740)

$$\begin{aligned} H_c &= -3.428 \text{ kg-cal/gram} \\ &= (-3.428)(240.17) = -823.3 \text{ kg-cal/gm-mole} \end{aligned}$$

b. Combustion of TEGDN:



c. Heat of Formation:

$$H_f, \text{TEGDN} (l) = 6(-94.40) + 6(-68.36) - (-823.3)$$

$$= -153.3 \text{ kg-cal/gm-mole}$$

APPENDIX "B" (Continued)

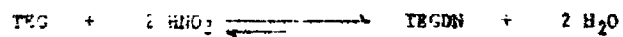
3. Heat of Reaction:

a. Heats of Formation:

$$(1) \text{ H}_2, \text{ HNO}_3 (l) = -42.35 \text{ kg-cal/gm-mole (MacDougall)}$$

$$(2) \text{ H}_2, \text{ H}_2\text{O} (l) = -68.36 \text{ kg-cal/gm-mole (MacDougall)}$$

b. Reaction:



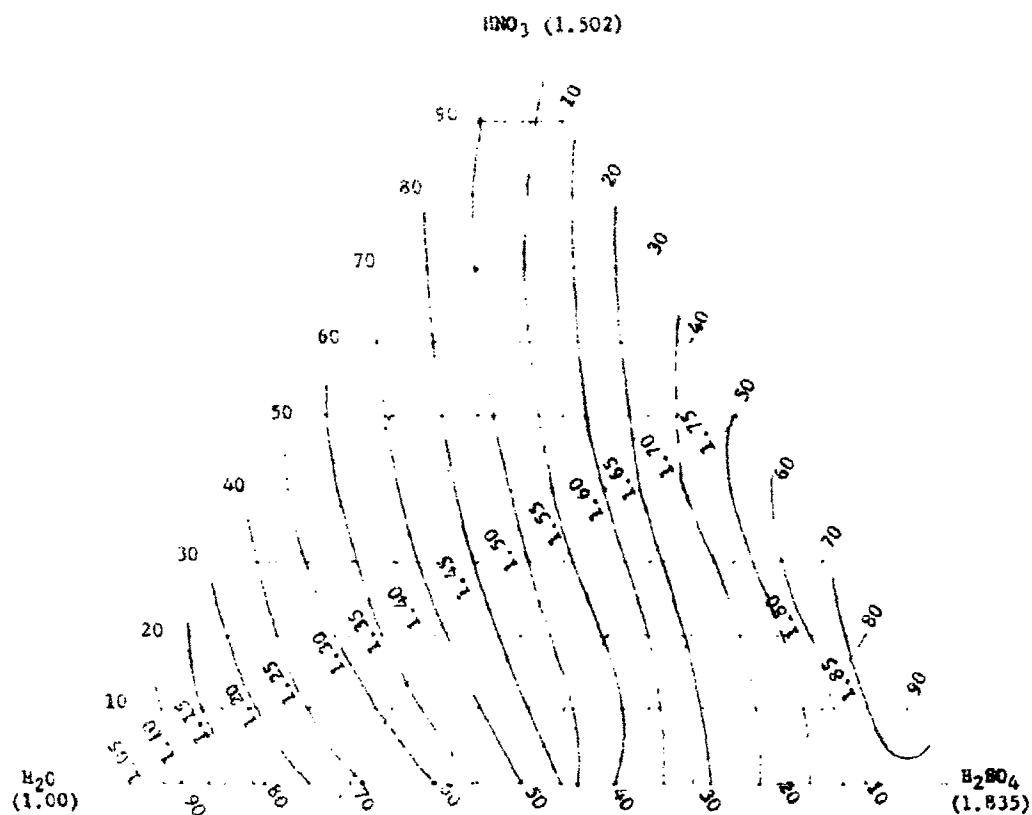
c. Heat of Reaction:

$$\Delta H^\circ = (-193.7) + 2(-42.35) - (-153.3) - 2(-68.36)$$

$$\Delta H^\circ = -11.6 \text{ kg-cal/gm-mole of TEGDN formed}$$

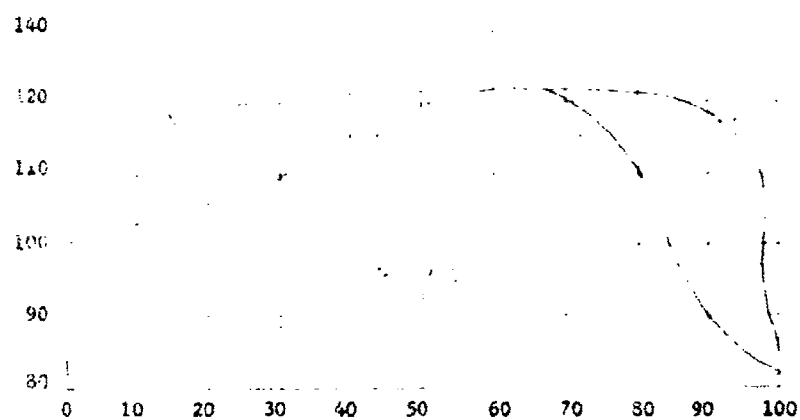
APPENDIX C

DENSITIES OF MIXED ACIDS AT 18°C.



APPENDIX "D"

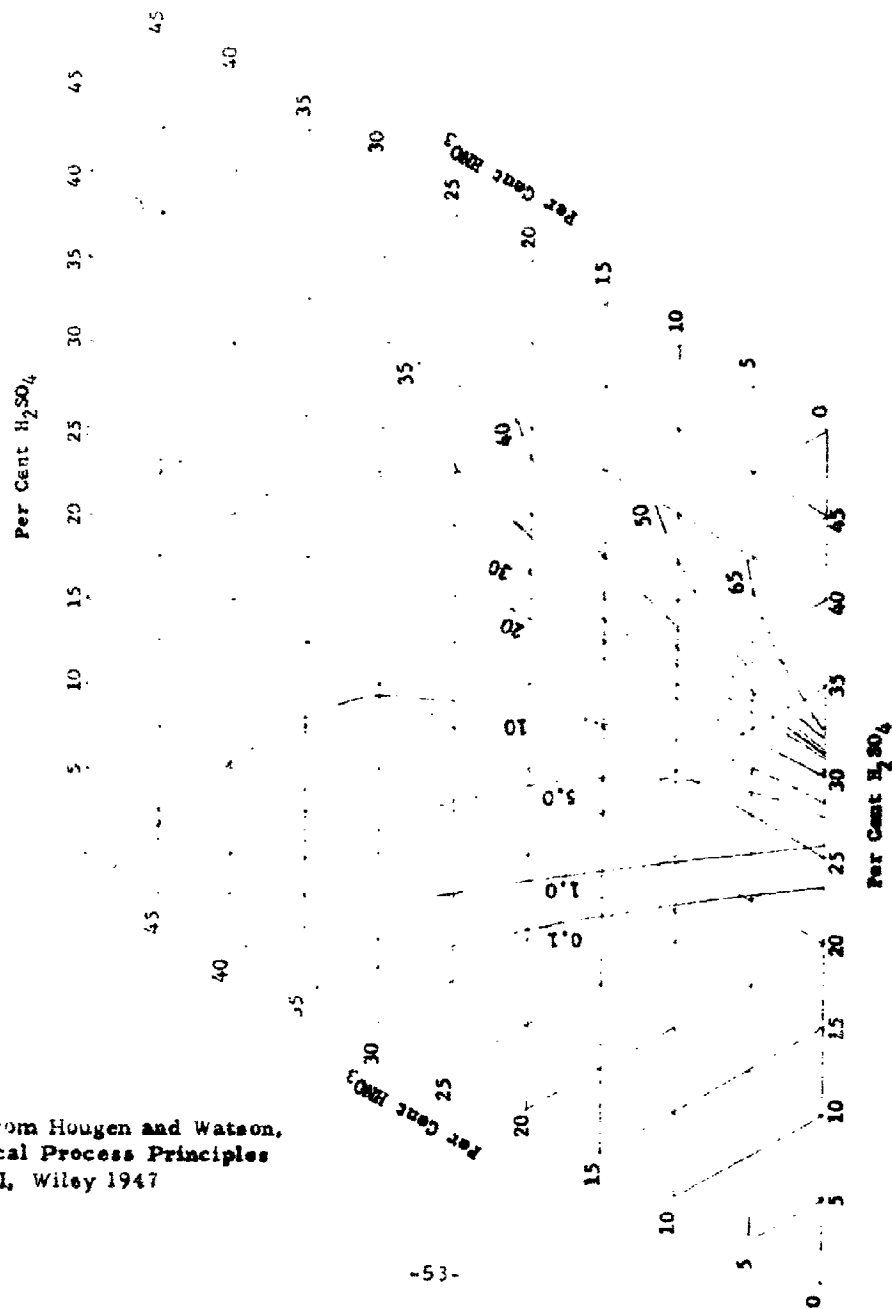
VAPOR-LIQUID EQUILIBRIUM FOR AQUEOUS NITRIC ACID



M is maximum boiling point at 122°C. and 68% nitric acid

APPENDIX "E"

RELATIVE ACTIVITY COEFFICIENTS OF MIXED ACIDS



Data from Hougen and Watson,
Chemical Process Principles
Part III, Wiley 1947

APPENDIX "T"

DEFINITION OF SYMBOLS

A	Second order reaction constant
w	Where reactants are present in equimolar amounts, the critical concentration of either in a second order reaction
x	Molar concentration of either product of a second order reaction
T	Temperature, absolute
K_a	Equilibrium constant of TEG-TEGDN reaction in activities
a_i	Activity (effective concentration) of a substance in equilibrium
K_a'	Equilibrium constant of TEGDN-TEGDN reaction in activities
K_a''	Equilibrium constant of TEG-TEGDN reaction expressed in activities
K_r	Equilibrium constant TEG-TEGDN reaction in terms of mole fractions
n	Total number of moles of all substances in the equilibrium
n_i	Mole fraction of a substance in the equilibrium
K_c	Equilibrium constant of the TEG-TEGDN reaction expressed in mole fractions with the activity of the "pseudo nitric acid" substituted for HNO_3 .
A	The effective activity of the nitric acid species present in the equilibrium at a particular mixed acid composition
i	Moles of Nitric Acid present at the beginning of the reaction
v	Moles of Sulfuric Acid at the beginning of the reaction
w	Moles of TEG present at the beginning of the reaction
x	Moles of water present at the beginning of the reaction
$\%C$	Mole per cent of a reactant at the beginning of the reaction
$\%P$	Mole per cent of a reactant or product
S	Number of moles of all substances present at beginning of reaction
Y	Number of moles of TEGDN formed at any point in the reaction
K_e	Constant of equilibrium for the TEG-TEGDN reaction where the constant activity of TEGDN is incorporated into K_a .
K_e'	Equilibrium constant of the sulfation reaction in terms of the activities of both reactants and both products
K_e''	Equilibrium constant of the sulfation reaction with the constant activity of the sulfate incorporated into K_e'
C	Equilibrium constant for the simultaneous equilibria between substances in the sulfation reaction and in the nitration reaction. Mathematically: K_e times K_e'
C'	Equilibrium constant for the simultaneous equilibria of sulfation and nitration reactions where C' is K_e divided by K_e'
ΔH°	Heat of reaction referred to the ground state
R	The universal gas constant
E	Constant of integration

FOR ERRATA

AD **258 435**

THE FOLLOWING PAGES ARE CHANGES

TO BASIC DOCUMENT

AD 358434
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August 16, 1961

Commanding Officer
U.S. Army Ordnance District, St. Louis
4300 Goodfellow Boulevard
St. Louis 20, Missouri

Subject: Errata Sheet - Final Report dated June 15, 1961
Contract DA-23-072-501-ORD-48
Development Study for Improvement of the Manufacturing Process for Triethyleneglycoldinitrate (TEGDN)

Page 27 Figure 5 is incorrectly labeled Figure 6.

Page 38 The 14th item (or run) from top of page should be corrected to Acid Mix H instead of 15 and run No. 15 where there is an omission.

Page 45 Line 8 should refer to Section IV c instead of V c as shown.

We wish to thank Picatinny Arsenal for pointing out these errors and hope no one has been inconvenienced to a great extent.

Propellex Chemical Division
Chromalloy Corporation

R. A. Cooley
R. A. Cooley
Executive Vice President

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