TECHNICAL REPORT 4871

CONVERSION OF GUANIDINE NITRATE TO NITROGUANIDINE WITH RECYCLE OF SPENT ACID

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OCTOBER 1975

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DOVER, NEW JERSEY

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report 4871	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Conversion of Guanidine Nitrate to Nitroguanidine with Recycle of Spent Acid		5. TYPE OF REPORT & PERIOD COVERED Interim
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Maurice Warman, Stanley Semel, John Leccacorvi, Rocco Motto, Richard Hutchinson		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Feltman Research Laboratory Picatinny Arsenal Dover, N.J. 07801		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE October 1975
		13. NUMBER OF PAGES 42
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Nitroguanidine	Recycled Spent Acid
Guanidine Nitrate	Ammonium Sulfate
Guanidine Sulfate	Sulfuric Acid

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Hercules Incorporated has designed a production facility to synthesize nitroguanidine and concentrate the spent acid for recycle. The program herein described was undertaken to verify the design criteria set forth by Hercules and to study parameters affecting the nitration and distillation of the spent acid.

It was found that a 94-96% conversion of guanidinium nitrate to nitroguanidine can be obtained using a sulfuric acid to sulfuric acid plus water ratio of 0.94. Vacuum distillation of the spent acid @ 50mm Hg with a hold

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time of one hour @ 100°C resulted in good conversion of the dissolved guanidine moiety to guanidine sulfate without decomposition to ammonia. By minimizing the ammonium salts formed, only a 5-10% bleed stream of the recycled acid would be required.

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FOREWORD

This program was initiated by the Picatinny Arsenal
Manufacturing Technology Division (MTD) and assigned to
the Feltman Research Laboratory (FRL). It was intended
to obtain required additional technological data in the
concentration and recycling of sulfuric acid for the
nitration of guanidine nitrate to nitroguanidine. This
information is to be used for establishing this phase
of the nitroguanidine facility project #5752632 for the
Sunflower AAP @ Lawrence, Kansas. This laboratory effort
was initially programed in the MM&TE project (#5744169)
to establish a greater reliability of this phase both
for the design criteria and final engineering design
stages of the facilities project.

This report is a compilation of data accumulated during
the initial phase of the program (13 Jan 75 - 30 July 75). The
second phase, to commence shortly, will encompass both the
completion of the parametric study under batch conditions and
the operation of a bench scale, continuous concentration system.

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INTRODUCTION

During the 1950's, comprehensive studies on the conversion
of guanidine nitrate (GN) to nitroguanidine (NQ) were conducted
by Dr. Pryde and coworkers at Waltham Abbey, Essex, England
(ERDE) (Ref 1) and in this country by Stamford Laboratories,
Research Division of the American Cyanamid Company (Ref 2).
Based, in part, on the laboratory data generated by these
studies, Hercules Incorporated designed a continuous process
nitroguanidine production facility to be built at Sunflower
AAP. A flow sheet of the proposed Hercules design for the NQ
process appears in Appendix C. The purpose of the work reported
herein was to verify, on a laboratory scale, the Hercules process
design for converting guanidine nitrate to nitroguanidine and
for recycling the resulting spent acid.

In the process proposed by Hercules, 94% sulfuric acid*
is used to dehydrate guanidine nitrate to produce nitroguanidine:

$$\overset{\overset{\displaystyle NH}{\displaystyle \|}}{H_2NCNH_2} \cdot HNO_3 \xrightarrow{\hspace{1cm} H_2SO_4 \hspace{1cm}} \overset{\overset{\displaystyle NH}{\displaystyle \|}}{H_2NCNHNO_2} + H_2O$$

Guanidine Nitrate   Nitroguanidine
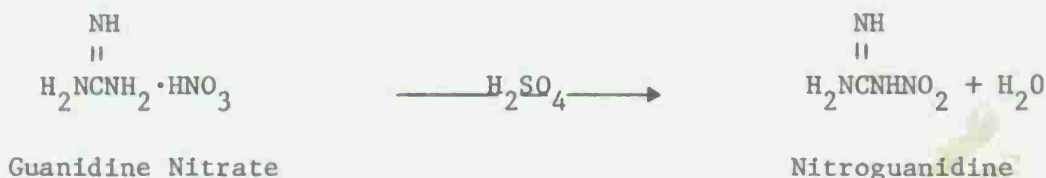
The NQ product is recovered by diluting the sulfuric acid with
water to 25%, cooling the mixture to 10°C, and filtering the
NQ from the spent acid. The crude NQ is then purified by
recrystallization from water. In the conventional commercial
process, the spent acid filtrate is neutralized and discarded.
In the proposed process, the spent acid is concentrated under
vacuum and reused. A critical aspect of the spent acid
concentration is the fate of the dissolved organic compounds
($\sim 0.7\%$ GN and $\sim 0.8\%$ NQ). Under desired plant conditions the
GN and NQ are converted to guanidine bisulfate which upon
recycle and reaction with nitric acid contributes to the over-
all yield of nitroguanidine. Under unfavorable conditions
the GN and NQ degrade to ammonium salts. A 5% acid bleed
stream is, therefore, specified to maintain the ammonium salts
at a fixed level of 19% in the acid feed stock.

*Throughout this report, the percent acid is calculated on an
acid-water basis disregarding the dissolved salts.

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In both the British and Cyanamid laboratory work, 96-98% sulfuric acid was used to dehydrate the guanidine nitrate to nitroguanidine. The acid filtrate was concentrated under vacuum, fortified with sulfuric acid, and reacted with fresh guanidine nitrate and nitric acid. The cycle was repeated a number of times to observe NQ yield, the build-up of ammonium salts, and the decomposition of dissolved GN and NQ during concentration. NQ yields of 96 to 98% were obtained, and acid purges of 5% and less were required.

Areas of primary concern in which the Hercules design conditions deviate from prior laboratory experience are the concentration of sulfuric acid and the quantity of nitric acid used in the nitration reaction, the conditions for spent acid concentration, and the size of the recycled acid bleed stream.

Hercules, to avoid potential corrosion problems associated with high temperature and acid concentration, chose to dehydrate the guanidine nitrate with 94% sulfuric rather than the 96 to 98% sulfuric acid used in previous work. In the proposed process a stoichiometric quantity of nitric acid is reacted with the guanidine bisulfate in the recycled acid whereas in the previous work 1.7 times the stoichiometric amount of nitric acid was employed. Finally, concentration of the spent acid employing temperature and pressure staging varied from previous laboratory experience.

The goal of the present work was to observe the collective effect of these apparently minor changes on product yield, purity, and acid bleed stream under expected plant conditions. The experiments were conducted batchwise, a deviation from the continuous plant process, a condition imposed by the scope of the study.

EXPERIMENTAL RESULTS

The laboratory procedure was based on the Hercules process design material balance and consisted of reacting guanidine nitrate containing 1% ammonium nitrate impuity with sulfuric acid (94% H_2SO_4) at 40°C for 140 minutes. The resulting solution was then diluted to 25% H_2SO_4 by the addition of the NQ wash water from the previous cycle, cooled to 10°C, and filtered to remove the precipitated NQ. The spent acid filtrate was concentrated under vacuum to be used in a subsequent nitration. The recovered acid was analyzed for H^+, NH_4^+, and water (See Appendix A). The remainder, presumably guanidine sulfate, was determined by difference. The NQ cake was washed by slurrying in water, filtered and dried. The wash water was saved for use in the next dilution.

Preliminary batch runs using fresh acid with 25g GN were conducted to gain experience in the preparation of NQ as shown in Table I. Nitroguanidine yields of 83% were obtained without the addition of nitric acid (Runs 2 and 3). Upon the addition of 2.1g of nitric acid, the NQ yield increased to 86% (Run 6). The effect of nitric acid on yield was consistent with the English results. Under plant conditions, ammonium sulfate $[(NH_4)_2SO_4]$ or bisulfate $[(NH_4)HSO_4]$ builds up from the ammonium nitrate impurity in the GN and the degradation of guanidine nitrate and nitroguanidine in the spent acid during concentration [1,2]. A series of runs was conducted to observe the effect of ammonium sulfate on NQ yields. In going from zero to 20% ammonium sulfate the NQ yield decreased by only 2-3% (Runs 7-12). The present plant design calls for an ammonium sulfate level of 19.2% in the acid feed stock. Thus, the effect of ammonium sulfate on NQ yields appeared minimal. The low yields of NQ in the preliminary runs, relative to the quantitative yields predicted by the Hercules process design, resulted from solubility losses of GN and NQ in the spent acid filtrate; recycle of the spent acid was expected to recover these losses.

Following the preliminary batch runs using fresh acid, a series of runs using recycled acid was made to test the Hercules flow-sheet conditions as depicted in Table II. The conditions used varied from those of Hercules in one aspect: the first stage concentration was conducted at 50mm Hg rather than at 130mm Hg in order to expedite the batch concentration of the acid in the laboratory.

[1] Material balances and concentrations are based on guanidine sulfate (Gu_2SO_4) and ammonium sulfate, although the salts may exist as bisulfates.

[2] Refer to Appendix B for the decomposition reactions.

The average yield of NQ obtained in Series 15 was 86% -
far below the predicted yields of 99+%. The amount of
guanidine sulfate in the recycled acid increased from 1.7g
in Run 15A to 7.8g in Run 15G. This result and the low NQ
yields obtained indicate that, although the GN and NQ were
largely preserved during concentration, they were not converted
to NQ during the reaction step. Moreover, it was observed that
as the level of GN and NQ built up, the quantity of ammonium
sulfate produced per cycle increased, see Figure 1. Thus, the
recycle of large quantities of guanidine compounds led to
increased decomposition rather than to increased NQ yields.

The British obtained NQ yields of 98-99% using 98% recycled
acid, and Cyanamid obtained 96% yields using 96% recycled acid.
In both studies an amount of nitric acid equal to the weight of
guanidine sulfate in the recycled acid was added to the reaction
mixture. Series 15, following Hercules' proposed operating
conditions, was conducted using less concentrated sulfuric
acid and smaller amounts of nitric acid than in the two previous
studies. These two parameters were investigated in series 16,
17 and 18 in an attempt to improve the yields of NQ.

Three concentrations of nitric acid were investigated in the
laboratory. An amount equal to 1.1 times the stoichiometric
quantity of nitric acid based on the guanidine sulfate in the
recycled acid resulted in an average NQ yield of 95% (Runs 17-17D,
Table III). An increase in HNO_3 to 1.7 times the stoichiometric
requirement in one instance appeared to increase the NQ yield
from 95% (Run 17C) to 97% (Run 17I). These two runs were
compared because the amounts of guanidine sulfate in the
recycled acids were equivalent. A large excess of nitric acid,
about 3 times the stoichiometric amount, did not significantly
increase the yield over that from 1.7 times the stoichiometric
amount (Runs 17E and 17F). Under the condition of increased
sulfuric acid strength, 96-98%, Table IV, nitric acid in excess
of the stoichiometric amount produced no increase in NQ yield.

The strength of sulfuric acid added to the reaction mixture
was varied from the flow-sheet condition of 94%. Using
recycled acid concentrated to 97%, yields of NQ greater than
100% were obtained in Runs 15H, 15I and 16, Table IV. Yields
in excess of 100% were due to conversion of the guanidine
salt in the recycled acid to product. Under conditions of low
nitric acid, increasing the strength of reaction acid
increased the yield of NQ (compare Runs 15H-15J, Table IV
and Runs 15-15G, Table II). When a stoichiometric amount of
nitric acid was used, increasing the sulfuric acid strength
from 94% to 97% effected a 2% increase in NQ yield (Runs 17-17D,
Table II versus Runs 16-16D, Table IV).

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Concentration of the recycled acid is a critical step in the proposed process. The British determined that although GN and NQ were unstable in hot sulfuric acid (above 100°C), guanidine sulfate and/or bisulfate were stable up to 200°C in 98% sulfuric acid. Furthermore, they determined that optimum conversion of GN and NQ to guanidine sulfate occurred at sulfuric acid concentrations of 70-75% and temperatures of 90-95°C. Reduced pressures were also required to remove the nitric acid released during the reaction and, thereby, shift the equilibrium in the desired direction. The British felt that the conditions for concentrating the acid from 25% to 70% were not critical providing the temperature did not exceed 100°C. In the proposed design, the acid is concentrated in three stages at pressures of 130, 50 and 20mm Hg. The size of the acid bleed stream is determined by the decomposition of the GN and NQ which, in turn, is dependent on the conditions of concentration.

Utilizing a pressure of 50mm Hg for stages one and two and a pressure of 20mm Hg for stage three, a stoichiometric amount of nitric acid, and 94% sulfuric acid, the acid bleed stream ranged from 5 to 12% and averaged 9% (Runs 17-17D Table III.) Under similar conditions, but utilizing 130mm Hg for the first stage concentration, the acid bleed stream varied from 9 to 11% and averaged 9% (Runs 18E-18G, Table III.) For strong sulfuric acid (97%) the acid bleed stream averaged 5 to 7% under various conditions of concentration, Table IV. In view of scatter in the data, no significant effect of the first-stage pressure on the size of acid bleed stream was observed.

The amount of nitric acid was observed to affect the size of the acid bleed stream and the level of guanidine sulfate in the recycled acid. For Runs 17E and 17F, Table III and Runs 18A-18D, Table IV, utilizing a large excess of nitric acid, the acid bleed stream averaged only 5%. The amount of guanidine sulfate resulting from the runs was also significantly less than in other runs where less nitric acid was used. It is suspected that high nitric acid favors decomposition of the GN and NQ to N_2O rather than to ammonia. Although the level of GN and NQ in the recycled acid is reduced, the excess nitric acid converts essentially all of the guanidine sulfate to GN during the reaction step, and high yields of NQ are obtained.

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A precipitate was observed to form during the second stage of the batch acid concentration accompanied by frothing and gas evolution. The foam constituted less than ten percent of the liquid volume. Both the foam and precipitate disappeared later in the distillation as the temperature approached 110-120°C. In runs where the quantity of ammonium sulfate increased significantly, indicating drastic decomposition of the guanidine molecule, no precipitate or foam was observed. It was theorized that the precipitate and foam were related to the conversion of GN and NQ to guanidine sulfate and nitric acid. The precipitate could have been guanidine sulfate which was insoluble under the conditions of the middle stage but soluble in the more concentrated acid.

Unexpectedly high acid concentrations (98+%) were obtained from the vacuum distillation procedure. Concentrations were calculated assuming that the ammonium and guanidinium salts existed as the sulfates. To test the apparatus and the analytical technique, a sample of 93.5% H_2SO_4 was heated to 170°C at 20mm Hg and held for 90 minutes. The final concentration was 94.3% which corresponds to handbook data for sulfuric acid-water mixtures. A synthetic mixture of 93.6% H_2SO_4 containing 19% ammonium sulfate was concentrated under the same conditions. The resulting acid concentration was 99.2% H_2SO_4. Another synthetic, simulating spent acid with NQ and GN present, was similarly concentrated and resulted in 98.1% sulfuric acid. To further elucidate the effect of ammonium salts on the boiling point of sulfuric acid, boiling point curves were experimentally obtained for the $H_2SO_4-H_2O-(NH_4)_2SO_4$ system at 20, 50, and 130mm Hg. The results are plotted in Figure 2. It can be seen that the presence of ammonium sulfate first causes a boiling point elevation at low acid concentrations and then a depression of the boiling point at higher acid concentrations.

It is suspected that the ammonium salt in concentrated sulfuric acid solutions is actually present as ammonium bisulfate and, therefore, the available free sulfuric acid is less than calculated. In Figure 3, the same acid concentration data is plotted, but concentrations are calculated based on the existence of ammonium bisulfate. This plot more closely corresponds to handbook data for sulfuric acid-water but still exhibits a depression of the boiling point at acid concentrations above 90%.

To complete the acid concentration phase of this project, the density and viscosity of simulated process spent acids were determined over the operating temperature range of the spent acid concentrator. The data is plotted in Figures 4, 5 and 6.

To determine if recycled acid would affect the purity of the crude NQ, samples of product NQ were sent to the Propellants Division, FRL, to be analyzed for purity and acid content. In all cases the purity was above 99% and the acid content was about 0.2-0.4%, calculated as H_2SO_4.

DISCUSSION

The strength of the sulfuric acid used in the nitration reaction was found to have a slight effect on NQ yield. Only a two percent increase in yield was observed in going from 94% sulfuric acid to 97% acid using a stoichiometric amount of nitric acid. The combination of high strength sulfuric acid and large amounts of nitric acid may raise the NQ yield to 98%. However, the potential corrosive effect of higher strength acid would have to be investigated before the option could be employed.

The amount of nitric acid added to the nitration reaction had an effect on both yield and the size of the acid bleed stream. The proposed design quantity of nitric acid, 4.5 tons/day, was found to be insufficient to convert the guanidine sulfate to NQ on a laboratory scale operation. A build-up of GN and NQ in the recycled acid stream was observed in laboratory experiments conducted during this program. Utilizing 1.1 to 1.7 times the stoichiometric quantity of nitric based on the amount of guanidine sulfate present resulted in NQ yields of 95 to 97%. A large excess of nitric acid (ca. 3 times stoichiometric) reduced the size of the acid bleed stream from approximately 10% to 5%. Large amounts of nitric acid appeared to decompose the GN and NQ in the recycled acid to N_2O rather than ammonia, thereby reducing the build-up of ammonium sulfate and the required acid bleed stream. The plant should be designed to handle a range of nitric acid feed rates to allow for changes in the quantity of Gu_2SO_4 and/or a higher than stoichiometric ratio of HNO_3 to Gu_2SO_4 (ca. 5-10 Tons/day nitric acid).

The conditions of acid concentration were varied to observe the effect on GN and NQ decomposition. No significant change in the size or composition of the acid bleed stream was observed when the pressure during stage one concentration was varied from 130mm Hg to 50mm Hg. However, preliminary batch experiments whereby the spent acid was flashed under plant conditions indicated that more decomposition occurred at 130mm Hg than at 50mm Hg. To be conservative, the plant should be designed to operate at a pressure of 50mm Hg in the first stage concentrator rather than at the present proposed design of 130mm Hg.

The presence of ammonium salts has a significant effect on the boiling point of the recycled acid. For instance, a final sulfuric acid concentrator temperature of 135-140°C rather than the preliminary design value of 170°C produced 94% sulfuric acid. To maintain the design profile of acid concentration, the first stage

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concentrator should operate at 90°C at 130mm Hg or 80°C at 50mm Hg, the middle three concentrators at 90°C, 95°C, and 100°C @ 50 mm, and the final two concentrators at 125°C and 135°C @ 20 mm Hg. In view of the lower boiling temperatures, it may be possible to operate the last concentrator at 50mm Hg rather than at the design value of 20mm Hg. This change would reduce capital and operating costs and, therefore, merits further investigation.

CONCLUSIONS

The following conclusions are to be recognized as being preliminary since all investigative work was conducted on a small, laboratory, batch experimental basis. It will be necessary to conduct a simulated continuous bench scale sulfuric acid demonstration system to establish reliable operating parameters since the plant facility design is based on a continuous operation under steady state conditions. However, these preliminary data are intended to facilitate the early design criteria parameters for the sulfuric acid concentration system.

1) Utilizing 94% H_2SO_4 for the GN to NQ reaction will result in a NQ yields of 94-96%.

2) Higher NQ yields (ca. 98%) may be attained using 98% H_2SO_4.

3) The plant should be designed to feed 10 tons/day nitric acid (or 1.5 to 2 times the stoichiometric requirement based on guanidine bisulfate).

4) The use of recycled acid does not affect the purity of the NQ product.

5) The first stage concentration should be designed to operate @ 50mm and 80°C.

6) The concentration of ammonium sulfate in the bleed stream will be between 20 and 22% under steady state conditions.

7) To maintain a 19% ammonium sulfate concentration in the recycled acid, a 5-10% bleed stream will be required.

8) Ammonium sulfate affects the boiling point of the $H_2SO_4-H_2O$ system. (See boiling point curves for recycled acid, Tables V through VII).

9) Concentrators should be designed to operate at higher than steady-state temperatures since the initially low ammonium sulfate concentration in the recycled acid during plant start-up results in higher acid boiling points.

REFERENCES

1)   Herbert, L.S., Jones, R.H., Pryde, A.W.H, "The Concentration and Re-Use of Spent Acid from the Nitration of Guanidine Nitrate", Explosives Research and Development Establishment Waltham Abbey, Essex, England, Report No. 32/R/59, Feb. 1960.

2)   "Studies Relating to Effluent Disposal in Nitroguanidine Manufacture", Product Research Department, Stamford Laboratories Research Division, American Cyanamid Company, D.O.A. Ordnance Corps Contract No. DAI-30-069-501-ORD-(P)-1220, 8 Dec 1955.

3)   Williams, R.W., Stalcup, H.,Fauth, M.I., "Determination of Ammonium Salts in Acid Mixtures Containing Guanidine Salts," U.S.Naval Powder Factory, Silver Springs, Md., Memorandum Report No. 132,1 April 1957.

4)   Dingle, L.E.,Pryde, A.W.H., "The Decomposition of Picrite in Sulfuric Acid in Relation to Safety in Low-Ratio Nitration of Guanidine Nitrate", Explosives Research and Development Establishment, Waltham Abbey, Essex, England, Report No. 6/R/64, 12 Dec 1963.

5)   Pryde, A.W.H., Lester, H.T., Martin, T., "The Conversion of Guanidine To Nitroguanidine by Means of Sulfuric Acid and Oleum", Explosives Research and Development Establishment, Waltham Abbey, Essex, England, Ref. XR441/38, June 1949.

6)   "Nitroguanidine facility dwgs. MB-3, PD-4, PD-5, PD-6, PD-7", Hercules Incorporated, Wilmington, Delaware, 2 March 1973.

Table I

Nitration of GN Using Fresh Acid[1,2]

Run#	In			Out	
	Conc. H_2SO_4 (%)	HNO_3 (g)	$(NH_4)_2SO_4$ (g)	NQ (g)	(% Yield)
2	93.0	–	–	17.57	83
3	93.0	–	–	17.55	83
6	93.0	2.1	–	18.22	86
7	93.0	2.1	3.25	18.45	87
8	93.0	2.1	6.50	18.40	86
9	93.0	2.1	9.75	18.25	86
10	93.0	2.1	13.0	18.07	85
12	93.0	2.1	16.25	17.69	83

Notes 1) 25 g guanidine nitrate w/0.25 g ammonium nitrate added to all nitrations
2) 60.5 g H_2SO_4 used in all nitrations

Table II

Nitration of GN Using Recycled Acid, 93% H_2SO_4[1,2]

Run #	In				Out				Percent Bleed[4]
	Conc HSO_4 (%)	HNO_3 (g)	$(NH_4)_2SO_4$ (g)	Gu_2SO_4 (g)	NQ (g)	(% Yield)	$(NH_4)_2SO_4$ (g)	Gu_2SO_4 (g)	
15	92.9	2.1	12.4	–	18.0	84	14.1	2.1	–
15A	92.9	2.1	15.3	1.7	18.8	88	13.7	2.2	
15B	93.7	2.1	15.3	1.9	18.1	85	19.8	4.9	–
15C	92.9	2.1	15.7	3.9	19.7	93	14.8	5.6	0
15D	93.5	2.1	16.0	5.1	18.8	88	17.0	2.4	9
15F	93.6	2.1	16.4	6.6	17.8	84	16.9	8.4	5
15G	93.7	2.1	16.6	7.8	17.6	83	20.9	9.2	22

Notes:
1) 25 g guanidine nitrate w/0.25 g ammonium nitrate added to all nitrations
2) 60.5 g H_2SO_4 used in all nitrations.
3) Spent acid was distilled at 50 mm Hg and held at 100°C for one hour. The pressure was then reduced to 20 mm and distillation continued to 145°C.
4) The percent bleed is the weight percent of acid removed from the recycled sulfuric acid.

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Table III

Nitration of GN Using Recycle Acid, 94% H_2SO_4 [1,2]

| Run# | In | | | | Out | | | | |
	Conc.H_2SO_4 (%)	HNO_3 (g)	$(NH_4)_2SO_4$ (g)	Gu_2SO_4 (g)	NQ (g)	NQ (%Yield)	$(NH_4)_2SO_4$ (g)	Gu_2SO_4 (g)	Percent Bleed
17[3]	94.0	3.3	15.5	5.1	19.8	93	15.7	5.3	5.0
17A[3]	94.0	3.6	15.3	5.6	20.0	94	16.2	4.1	5.8
17C[3]	94.0	2.4	15.6	3.7	20.3	95	17.4	2.9	11.0
17D[3]	94.0	2.5	15.7	3.9	20.5	96	17.6	5.7	12.0
17E[3]	94.0	9.0	15.9	5.1	20.8	98	16.8	1.5	6.0
17F[3]	94.0	5.3	15.1	1.4	20.5	96	15.4	1.2	3.7
17G[5]	94.0	5.1	15.0	1.2	19.8	93	16.2	1.3	8.1
17H[4]	94.0	1.2	15.0	1.2	19.3	91	15.1	3.8	0.6
17I[4]	94.0	3.6	14.4	3.6	20.7	97	17.2	1.7	19.5
17J[4]	94.0	2.0	15.1	1.5	19.7	92	16.4	0.9	8.5
17K[4]	94.0	1.0	15.0	0.8	19.2	90	16.7	1.9	11.4
17L[4,6]	94.0	1.8	15.2	1.8	19.8	93	–	–	–
18E[5]	94.0	0.9	13.9	1.4	18.6	87	15.7	2.2	10.6
18F[5]	94.0	1.4	14.8	2.1	19.8	93	16.3	2.9	8.1
18G[4,7]	94.0	1.8	15.4	2.7	18.4	96	16.8	–	9.1

Table III (continued)

Notes: 1) 25 g guanidine nitrate w/0.25 g ammonium nitrate added to all nitrations.
2) 60.5 g H_2SO_4 used in all nitrations
3) Spent acid distilled as follows:

Temperature	Pressure	Hold Time
95°C	50mm	45 Min
100	50	45
110	50	45
140	20	90

4) Spent acid distilled as follows:

Temperature	Pressure	Hold Time
80°C	130mm	30 Min
95	50	45
100	50	45
110	50	45
140	20	90

5) Spent acid distilled as follows:

Temperature	Pressure	Hold Time
90°C	130mm	30 Min
95	50	45
100	50	45
110	50	45
140	20	90

6) Concentration of acid was not performed because program was terminated.
7) 22.5 g guanidine nitrate w/0.23 g ammonium nitrate added to nitration.

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Table IV

Nitration of GN Using 96-97% H_2SO_4 [1,2]

| Run # | In | | | | Out | | | | Percent Bleed |
	Conc H_2SO_4 (%)	HNO_3 (g)	$(NH_4)_2SO_4$ (g)	Gu_2SO_4 (g)	NQ (g)	NQ (% Yield)	$(NH_4)_2SO_4$ (g)	Gu_2SO_4 (g)	
15H[3]	97.7	2.1	15.8	7.0	21.5	101	16.6	6.9	7.0
15I[3]	97.0	2.1	15.7	6.0	21.3	100	15.7	5.7	2.0
15J[3]	96.0	2.1	15.7	5.3	21.0	95	17.1	5.2	11.0
15K[3]	95.0	2.1	15.7	4.9	19.6	92	16.7	6.9	8.0
16 [3]	97.5	5.6	15.5	6.4	21.5	101	15.9	3.9	4.0
16A[3]	96.8	2.1	15.2	3.9	20.0	94	15.9	5.5	6.0
16B[3]	97.7	3.2	15.5	5.3	20.9	98	15.9	4.9	4.0
16C[3]	97.3	2.8	15.5	4.8	20.0	94	16.3	4.7	9.0
16D[3]	97.1	2.8	15.3	4.4	20.0	94	15.9	5.3	6.0
18 [4]	96.0	5.5	15.2	3.0	20.9	98	19.1	1.4	20.9
18A[4]	96.0	3.6	14.7	1.1	19.6	92	15.3	0.9	5.2
18B[4]	96.0	3.4	14.7	0.8	20.2	95	15.5	0.3	6.5
18C[5]	96.0	2.8	14.5	0.3	20.3	95	15.5	1.7	5
18D[5]	96.0	4.1	14.0	1.6	20.5	96	14.5	1.4	5

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Table IV (continued)

Notes: 1)   25 g guanidine nitrate w/0.25 g ammonium nitrate added to all nitrations.
2)   60.5 g H_2SO_4 used in all nitrations
3)   Spent acid was distilled at 50 mm Hg and held at 100°C for one hour. The pressure was then reduced to 20 mm and distillation continued to 145°C.
4)   Spent acid was distilled as follows:

Temperature	Pressure	Hold Time
90°C	130mm	5 min
95	50	45
100	50	45
110	50	45
145	20	90

5)   Spent acid was distilled at 20mm Hg and held at 88°C for 90 minutes.

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Table V

Boiling Point Data for 130mm Hg

Percent				$H_2SO_4 / H_2SO_4 + H_2O$	B.P.
H_2SO_4	H_2O	$(NH_4)_2SO_4$	Gu_2SO_4		
37.82	49.75	11.81	0.62	0.432	75[1]
49.51	33.89	16.60	-	0.594	90[1]
50.46	33.06	15.86	0.62	0.604	90[1]
52.11	31.2	13.86	2.83	0.625	95[2]

Notes: 1) Data obtained from flash evaporator experiments using synthetic spent acids mixtures.
2) Spent acid from NQ Run # 764-287-50.

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Table VI

Boiling Point Data for 50mm Hg

	Percent			$\dfrac{H_2SO_4}{H_2SO_4+H_2O}$	B.P °C
H_2SO_4	H_2O	$(NH_4)_2SO_4$	Gu_2SO_4		
36.06	53.17	10.77	–	0.404	57.5
40.63	47.23	12.14	–	0.472	62.5
46.20	39.46	14.34	–	0.539	71.0
53.63	29.84	16.03	0.50	0 640	80.0[1]
52.95	32.02	15.03	–	0.623	81.5
58.15	23.24	18.61	–	0.714	93.5
59.82	20.30	19.76	–	0.744	98.0[2]
59.7	21.0	19.27	–	0.740	102.0
62.12	17.87	20.03	–	0.777	104.0[2]
60.03	20.81	19.16	–	0.743	104.5
61.40	17.40	20.62	0.58	0.779	105.0[2]
63.03	15.10	21.12	–	0.807	116.0[2]
63.78	12.83	20.29	3.10	0.833	117.0[2]

Notes: 1) Data obtained from flash evaporator experiment using synthetic spent acid mixtures.
   2) Spent acid from NQ Run # 764-287-50.
   3) All other data accumulated from synthetic spent acid mixtures.

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Table VII

Boiling Point Data for 20mm Hg

	Percent			$H_2SO_4/$	
H_2SO_4	H_2O	$(NH_4)_2SO_4$	Gu_2SO_4	$H_2SO_4+H_2O$	B.P. °C
43.06	42.37	14.57	-	0.504	64.5
48.40	35.15	16.45	-	0.579	71.7
54.53	27.44	18.13	-	0.665	78.5
59.38	19.71	20.91	-	0.751	88.0
63.22	15.00	21.78	-	0.808	102.6
65.75	11.48	22.77	-	0.856	119.0
74.95	3.17	20.31	1.57	0.959	140.0 [1]
75.40	2.00	20.70	1.90	0.974	145.0 [1]
69.97	1.32	19.18	9.52	0.981	150.0 [1]
70.10	5.38	24.52	-	0.929	153.5
70.85	5.10	21.51	2.54	0.933	157.0 [2]
71.48	3.90	23.91	-	0.948	158.0 [2]

Notes: 1) This data is for recycled acid.
2) Spent acid from NQ Run # 764-287-50.

Table VIII

Viscosity and Density of Recycled Acid

from Nitro-guanidine Production

Acid mixture: $(NH_4)_2SO_4/H_2SO_4 = 0.251$ [1]

$Gu_2SO_4/H_2SO_4 = 0.0576$ [1]

Sulfuric Concentration, $H_2SO_4+H_2O$ Basis, %	Density, 25°C g/cc	Temperature °C	Viscosity cp
25	1.16	25	1.57
65	1.52	47.5	6.02
		91.5	2.75
75	1.60	79.5	5.94
		99	4.16
85	1.67	80	9.92
		105	5.82
94	1.74	27	64.7
		85	10.4
		121	5.24

Note:
1) Values shown are weight ratios.
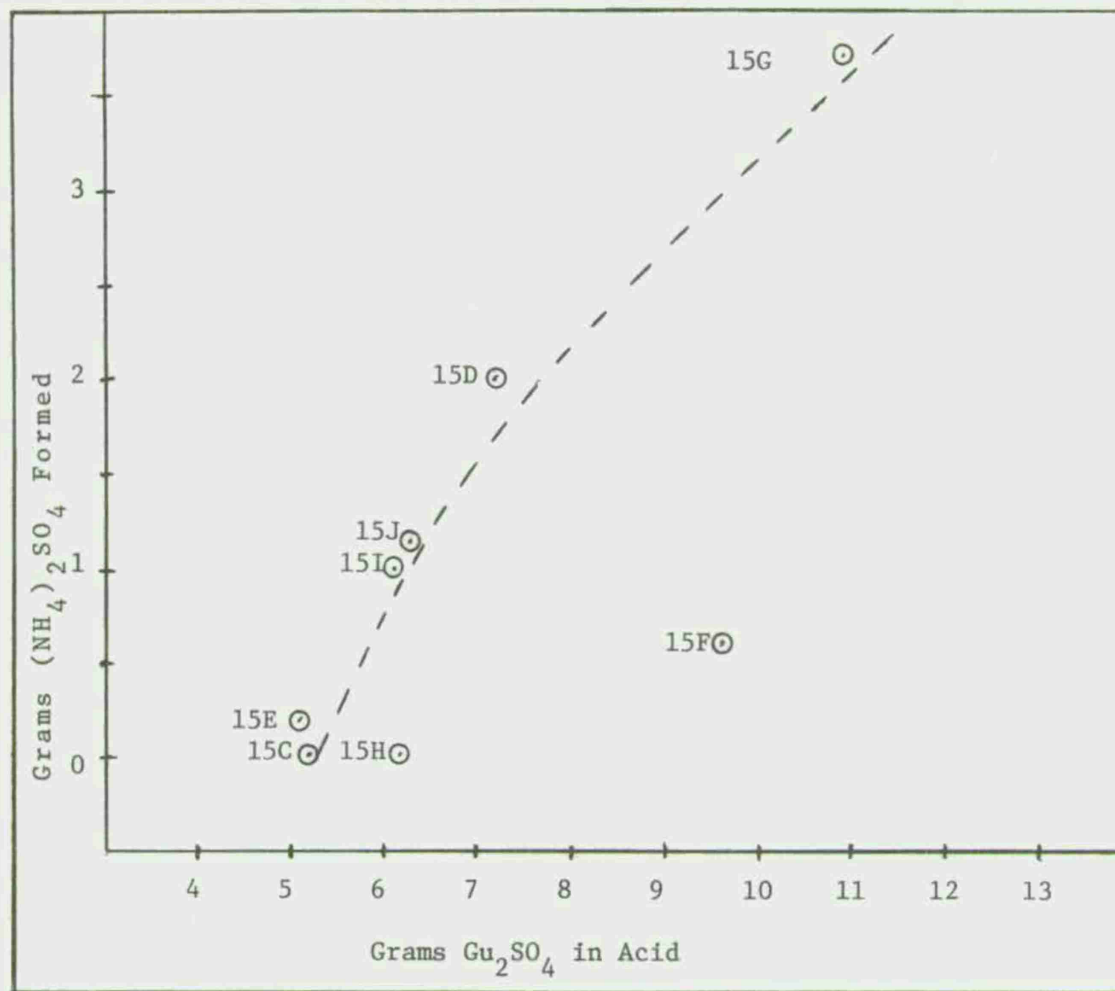
Figure 1

Grams $(NH_4)_2SO_4$ Formed vs Grams Gu_2SO_4 in Acid
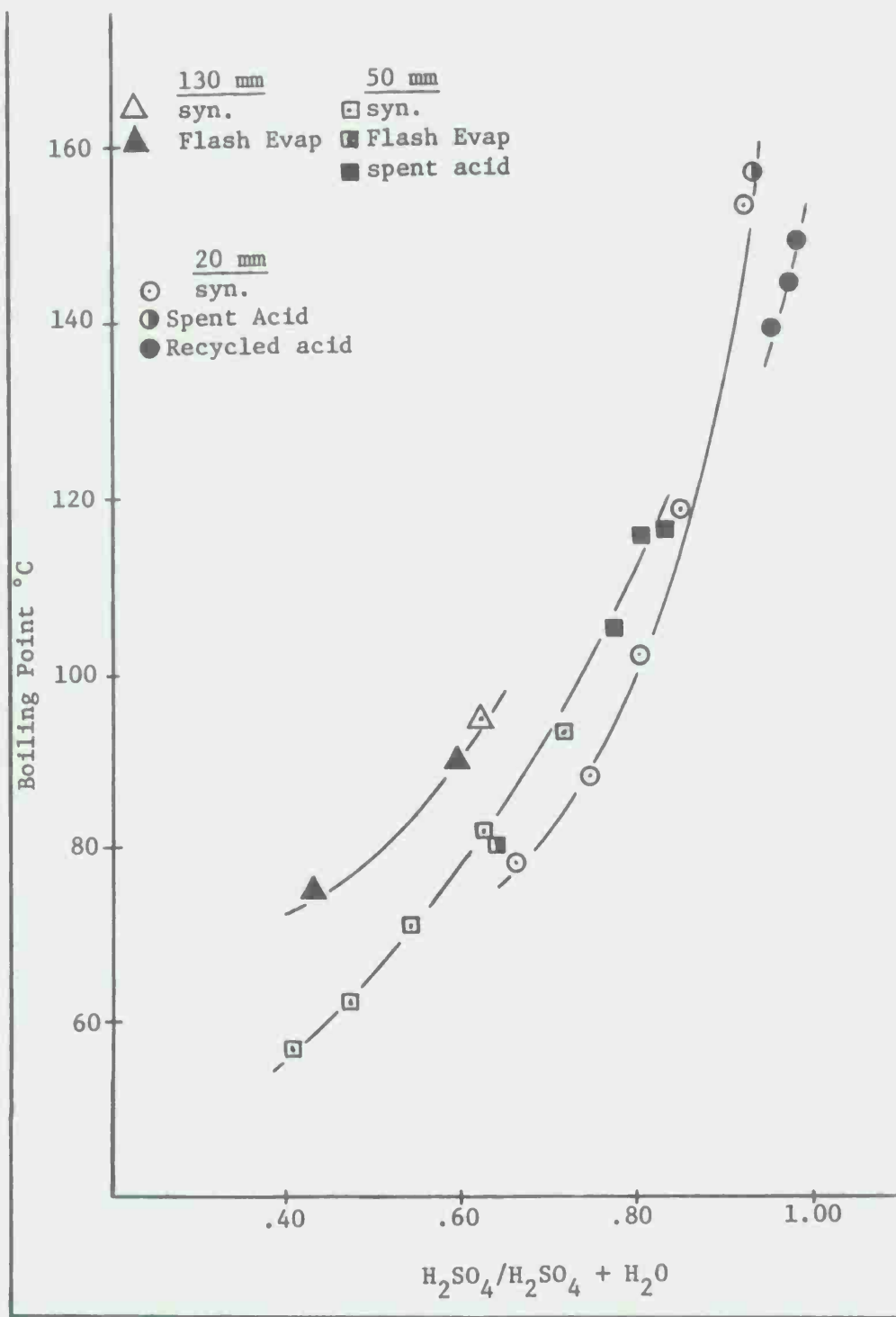
Figure 2

Boiling Point vs Acid Concentration

23
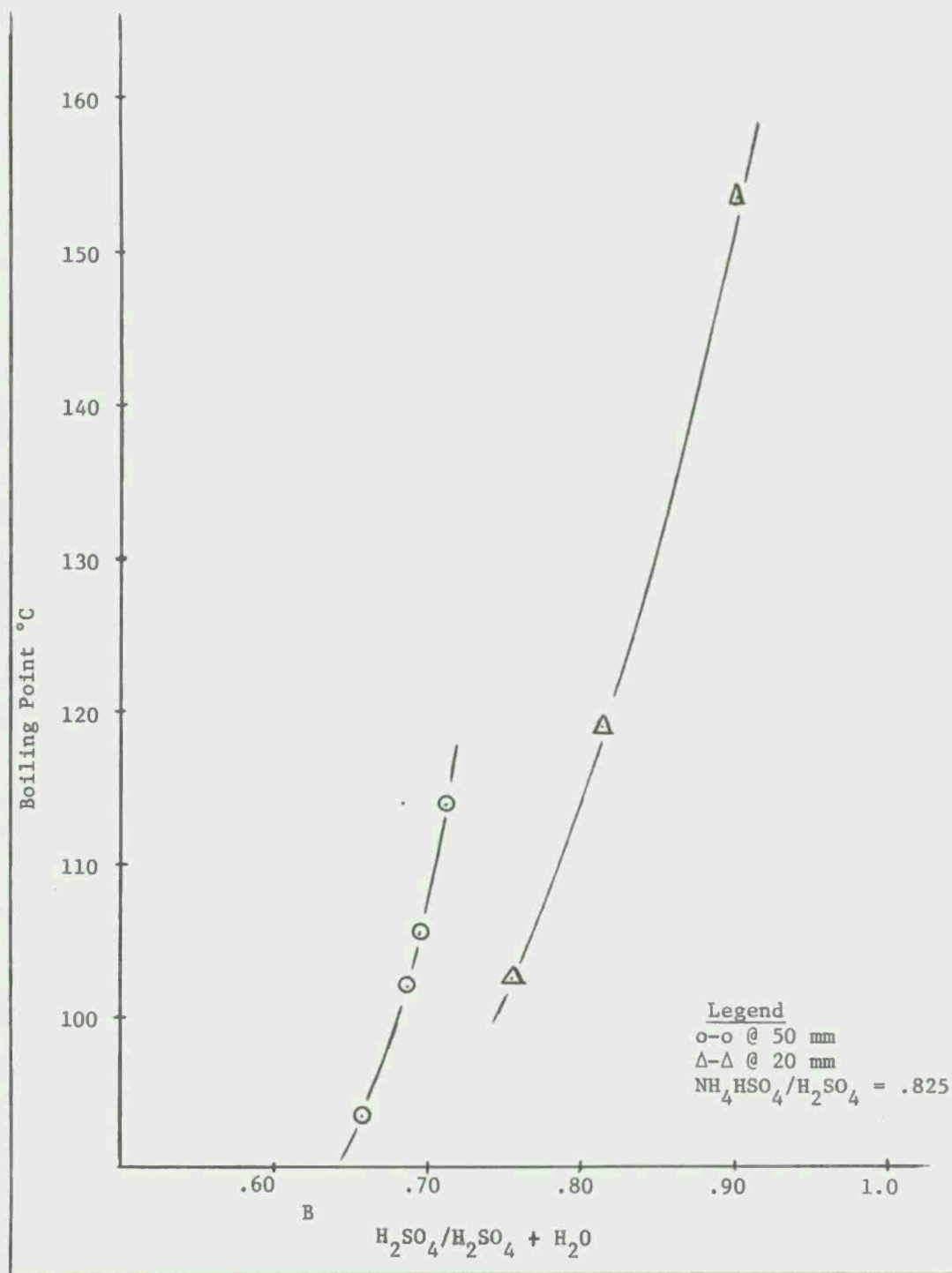
Figure 3

Boiling Point vs Acid Concentration
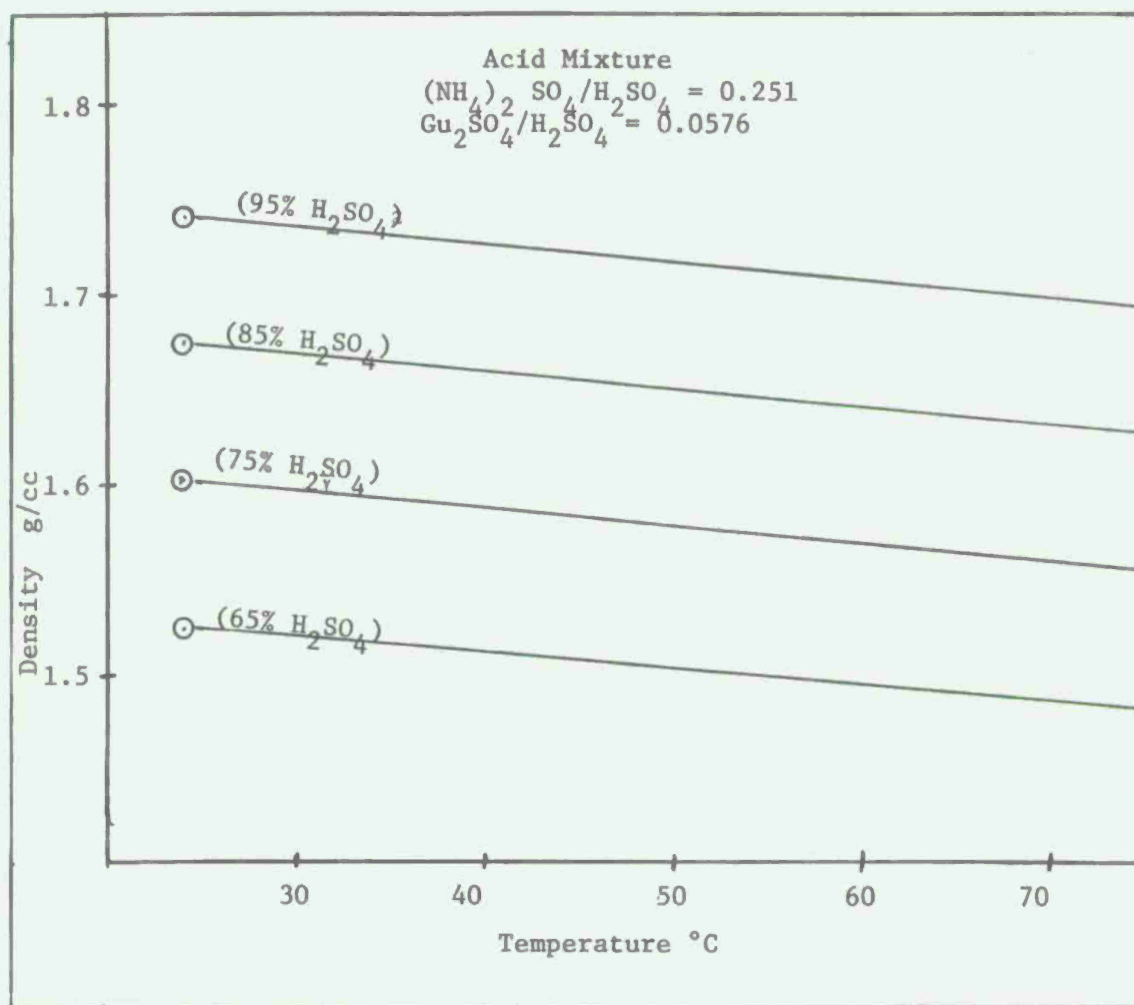
Figure 4

Density of Recycled Acid vs Temperature

Note:

These lines represent an extrapolation of data based on
handbook values.
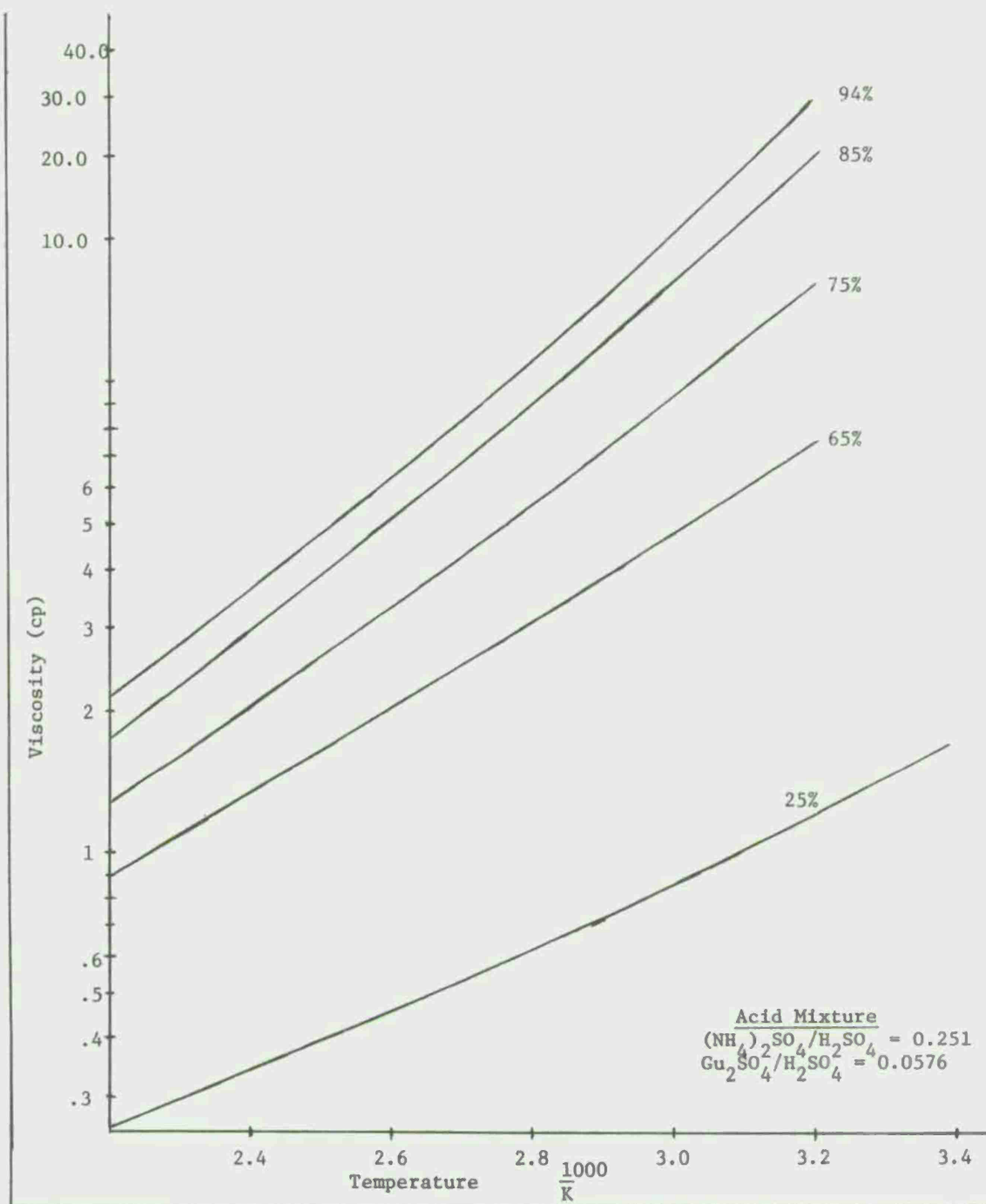
Figure 5

Log Viscosity vs Temperature
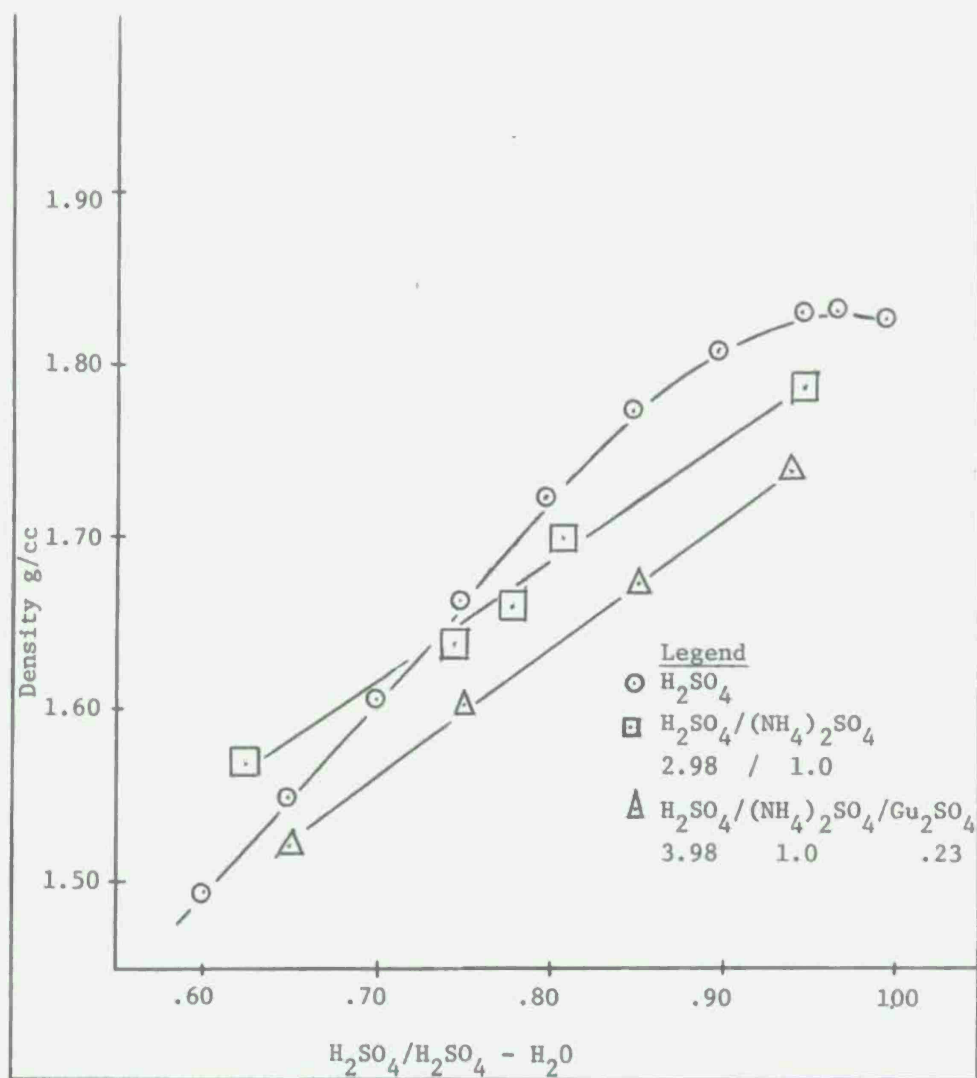
Figure 6

Density vs Acid Concentration

@

25°C

APPENDIX A

EXPERIMENTAL PROCEDURE

Nitration and Distillation

The recycled acid was analyzed to determine its composition. After bleeding the proper amount of acid in order to maintain an 18.66% $(NH_4)_2SO_4$ level in the fortified acid, concentrated sulfuric acid and water were added to result in a solution containing 60.5 grams H_2SO_4 at the desired acid strength. To this mixture was added a predetermined amount of nitric acid and the stirred solution was heated to 38°C. Twenty five grams of guanidine nitrate containing 1% ammonium nitrate was then added in portions. Although initial additions were exothermic, external heat had to be applied during latter additions to maintain the reaction temperature at 40°C for 140 minutes. At the end of this time, the solution was quenched by the rapid addition of the NQ wash water from the previous batch. An exotherm resulted with the temperature rising to 46°C followed by the formation of a copious precipitate of nitroguanidine bisulfate.. The application of external heat to elevate and maintain the temperature at 50-60°C insured the hydrolysis of the bisulfate to nitroguanidine. The mixture was cooled to 10°C and held at this temperature for one hour to minimize the dissolved NQ remaining in the spent acid. The crude NQ was filtered from the spent acid, which was saved for recycle. The crude NQ was then washed by slurrying in water (173 ml) for 30 minutes. It was collected by filtration and dried in vacuo over Drierite. The filtrate was saved for the next quench.

The spent acid was concentrated utilizing a three stage vacuum distillation technique in a 300 ml flask. The first stage, which raised the sulfuric acid concentration from 25 to 60%, was performed at 130 mm and 90°C. This temperature was lowered in subsequent distillations to 80°C. Other distillations were conducted under various pressures and temperatures trying to minimize the degradation of guanidine to ammonia. The second stage of the concentration was performed in three steps. During this stage, the acid concentration was increased to 79% and the guanidine nitrate and nitroguanidine were converted to guanidine sulfate. In all three steps the pressure was maintained at 50mm but the temperature was increased in increments from 95 to 100 to 110°C with a holding time of 45 minutes at each step. A

precipitate, accompanied by foam, formed during the first step but dissolved as the third step was approached. At this point, the acid was concentrated under the third stage conditions which were 140°C and 20mm Hg. The final temperature was varied to obtain the desired acid strength.

Viscosity

Ubbelohde viscometers were placed in a constant temperature bath and the time required for the acid level to change between two set points was recorded. The viscosity of various acid concentrations was determined over a temperature range.

Analytical

The hydronium ion was determined by titration with standard 1 N NaOH and calculated as H_2SO_4. The ammonium sulfate was determined by the U. S. Naval Powder Factory method (Ref 3) and the water by Karl Fisher titration. The remainder, presumably guanidine sulfate, was obtained by difference.

APPENDIX B

REACTIONS

Appendix B

These reactions describe the conversion of nitroguanidine to guanidine bisulfate (1) and the decomposition of nitroguanidine to ammonia and N_2O (2-5).

$$
\begin{array}{l}
NHNO_2 \\
| \\
C = NH + H_2O \rightleftharpoons \\
| \\
NH_2
\end{array}
\qquad
\begin{array}{l}
NH_2 \\
| \\
C = NH_2 \bullet HSO_4 + HNO_3 \\
| \\
NH_2
\end{array}
\qquad (1)
$$

Nitroguanidine   Guanidine Bisulfate

$$
\begin{array}{l}
NHNO_2 \\
| \\
C = NH \rightarrow \\
| \\
NH_2
\end{array}
\qquad
\begin{array}{l}
NH_2 \\
| \\
C = O + N_2O \\
| \\
NH_2
\end{array}
\qquad (2)
$$

Nitroguanidine   Urea

$$
\begin{array}{l}
NH_2 \\
| \\
C=O + HNO_3 \rightleftharpoons \\
| \\
NH_2
\end{array}
\qquad
\begin{array}{l}
NHNO_2 \\
| \\
C=O + H_2O \\
| \\
NH_2
\end{array}
\qquad (3)
$$

Urea   Nitro urea

$$
\begin{array}{l}
NHNO_2 \\
| \\
C=O \rightarrow NH_3 + CO_2 + N_2O \\
| \\
NH_2
\end{array}
\qquad (4)
$$

Nitro urea

$$
\begin{array}{l}
NH_2 \\
| \\
C=O + H_2O \rightarrow 2NH_3 + CO_2 \\
| \\
NH_2
\end{array}
\qquad (5)
$$

Urea

APPENDIX C

HERCULES PROPOSED FLOW SHEET

Process flow diagram — Nitroguanidine Facility, Nitroguanidine Manufacture & Acid Recovery Material Balance

Top row process units: NITRATION → DILUTION → CRUDE CRYSTALLIZATION → CRUDE FILTRATION → RE-PULP FILTRATION → RE-SOLUTION → PURE CRYSTALLIZATION → PURE FILTRATION → DRYER → PACKING

OLEUM

	T/D	%
40% OLEUM	7.0	94
HNO₃	0.4	6
	7.4	100

ABSORB IN DILUTION LIQUOR

VENT
HNO₃ 0.8
NQ 0.6

GUANIDINE NITRATE

	T/D	%
GN	53.8	98.4
AN	0.5	1.0
H₂O	0.3	0.6
	54.6	100.0

99% NITRIC ACID

	T/D	%
HNO₃	4.1	99
H₂O	0.1	1
	4.2	100.0

NOTE:— BETWEEN NITRATION & DILUTION NQ EXISTS AS NITROGUANIDINE BISULFATE

RECYCLE ACID

	T/D	%
H₂SO₄	123.0	69.2
H₂O	9.2	5.2
(NH₄)₂SO₄	34.0	19.2
GN·H₂SO₄	11.3	6.4
	177.5	100.0

NITRATOR SYRUP

	T/D	%
H₂SO₄	137.5	56.2
H₂O	17.5	7.2
(NH₄)₂SO₄	34.8	14.3
HNO₃	0.4	0.2
NQ	49.5	20.3
GN	4.4	1.8
	244.1	100.0

DILUTION SLURRY

	T/D	%
H₂SO₄	141.8	20.6
H₂O	454.0	66.3
(NH₄)₂SO₄	35.2	5.1
HNO₃	0.6	<0.1
NQ	50.4	7.3
GN	4.4	0.6
	686.4	100.0

CRUDE SLURRY

	T/D	%
H₂SO₄	141.8	21.6
H₂O	424.0	64.6
(NH₄)₂SO₄	35.2	5.1
HNO₃	0.6	<0.1
NQ	50.4	7.7
GN	4.4	0.7
	656.4	100.0

CRUDE WASH
H₂O 297.0
(NH₄)₂SO₄ 0.4
297.3

CRUDE FILTER CAKE

	T/D	%
NQ	45.9	70.0
H₂O	70.0	
NQ	0.9	
(NH₄)₂SO₄	SOME	

BOOSTER STEAM 50

EJECTOR STEAM 10
WATER VAPOR 30

TOTAL 90

RE-PULP

RE-PULP FILTER CAKE
NQ 45.9
H₂O 70.0

550 T/D

RE-PULP FILTRATE

DILUENT WATER 70

AMMONIA NH₃ 0.1

STEAM 42

RE-CRYSTALLIZATION FEED SOLUTION
NQ 46.9
H₂O 422.0

BOOSTER STEAM 120

EJECTOR STEAM 5
WATER VAPOR 64

WATER WASH H₂O 104 T/D

PURE SLURRY
NQ 45.4
H₂O 656.0

PURE FILTER CAKE
NQ 45
H₂O 30

EVAPORATION WITH EXHAUST AIR H₂O 30

BELT WASH H₂O 35

DRYER SCRUBBER

DRYER PRODUCT
NQ 45

PACKAGED PRODUCT TONS/DAY 45 NITROGUANIDINE

CRUDE FILTRATE

	T/D	%
H₂SO₄	141.5	23.2
H₂O	424.0	69.4
(NH₄)₂SO₄	35.1	5.8
HNO₃	0.6	<.1
NQ*	4.6	0.8
GN	4.4	0.7
*AS BISULFATE	610.2	100.0

CRUDE WASH FILTRATE
NQ 0.9
(NH₄)₂SO₄ 0.4

PURE FILTRATE
NQ 0.9
H₂O 207.0
(NH₄)₂SO₄ TRACE
NH₄HSO₄ TRACE

PURE FILTRATE
NH₄HSO₄ TRACE
(NH₄)₂SO₄ TRACE
NQ 1.0
H₂O 240.0

PURE FILTRATE
NH₄HSO₄ TRACE
(NH₄)₂SO₄ TRACE
NQ 1.5
H₂O 318.0

PURE FILTRATE
NH₄HSO₄ TRACE
(NH₄)₂SO₄ TRACE
NQ 3.4
H₂O 730.0

BELT WASH
NQ 0
H₂O 35

H₂O 438.0
H₂SO₄ 4.3

H₂O 209.0
H₂SO₄ 4.3

TO DILUTION & RECYCLE
H₂O 76.5
H₂SO₄ 4.3

H₂O 133.0
HNO₃ 0.2

TO NEUTRALIZER IN GN AREA

H₂O 202.0
HNO₃ 0.4

TO CALCIUM CARBONATE FILTER IN GN AREA

H₂O 335.0
HNO₃ 0.6

Acid recovery units: WEAK ACID STORAGE → LOW STAGE CONCENTRATION → MIDDLE STAGE CONCENTRATION → HIGH STAGE CONCENTRATION → COOLING → STRONG ACID STORAGE

LOW STAGE CONCENTRATION $\dfrac{H_2SO_4}{H_2SO_4+H_2O} \approx 60\%$

	T/D	%
H₂SO₄	141.5	50.8
H₂O	95.0	33.9
(NH₄)₂SO₄	35.1	12.5
NQ	4.6	1.6
GN	4.4	1.5
	280.6	100.0

MIDDLE STAGE CONCENTRATION $\dfrac{H_2SO_4}{H_2SO_4+H_2O} \approx 75\%$

	T/D	%
H₂SO₄	133.7	59.2
H₂O	44.5	19.7
(NH₄)₂SO₄	35.6	15.7
GN·H₂SO₄	12.1	5.4
	225.9	100.0

H₂O 55.0
HNO₃ 5.0

HIGH STAGE CONCENTRATION $\dfrac{H_2SO_4}{H_2SO_4+H_2O} \approx 94\%$

COOLING
H₂SO₄ 128.0
H₂O 9.7
(NH₄)₂SO₄ 35.9
GN·H₂SO₄ 11.9

CONDENSED STEAM 6.0

CONDENSED STEAM 4.5

CONDENSED STEAM 41.7

NORMAL 5% PURGE TO (NH₄)₂SO₄ MANUFACTURE 8 TONS/DAY CAN BE REDUCED BY LOWERING NH₄NO₃ IN GN FEED

PURGE
H₂SO₄ 5.8
H₂O 0.4
(NH₄)₂SO₄ 1.6
GN·H₂SO₄ 0.5
8.3

SAC PLANT ADDITIVE

NOTE: IN THE PRESENCE OF EXCESS SULFURIC ACID AMMONIUM BISULFATE EXISTS RATHER THAN AMMONIUM SULFATE. FOR CALCULATIONS AND ACCOUNTING PURPOSES AMMONIA IS CONSIDERED AS THE SULFATE.

AMMONIUM SULFATE MFG. PLANT NIC

Bottom units: CRYSTALLIZATION → SEPARATION → DRYING

NH₃ FOR (NH₄)₂SO₄ MFRG., APPROX. 2 TONS/DAY

(NH₄)₂SO₄ TO SALES APPROX. 8 T/D. CAN BE REDUCED TO <8 T/D BY LOWERING NH₄NO₃ IN GN THUS REDUCING NEED TO PURGE NH₄⁺, OR BY CRYSTALLIZING NH₄HSO₄ FROM ACID & RETURNING ACID TO STRONG ACID STORAGE.

LEGEND
——— SOLID OR LIQUID PHASE
- - - - VAPOR PHASE

NOTE: ALL QUANTITIES SHOWN IN T/D

THIS DRAWING HAS BEEN REDUCED TO ONE-HALF THE ORIGINAL SCALE

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