COPY NO. 6

1

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROP

ATI NO. 36157

CADO FILE COPY

4118

~~RESTRICTED~~

TECHNICAL REPORT NO. 261-45

NITROGUANIDINE - MANUFACTURE AND USE IN GERMAN PROPELLANTS AND HIGH EXPLOSIVE SHELLS

OCTOBER 1945

AD A953132

DTIC FILE COPY

DTIC
ELECTE
APR 13 1984
S D
E

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROP

UNCLASSIFIED

This document has been approved for public release and sale; its distribution is unlimited.

TP 270/P31

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N.Y.

File: A9-16(3)(40/Hn)

Serial: 1424

13 October 1945

~~R E S T R I C T E D~~

From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 261-45, Nitroguanidine - Manufacture and Use in German Propellants and High Explosive Shells - Forwarding of.

Enclosures: (A) (HW) Four (4) Complete copies of subject report as listed in distribution.
(B) (HW) One (1) set of negatives of photographs in subject report with copy No. 5 as listed in distribution.

1. Enclosures (A) and (B) are forwarded herewith.

2. CNO (OP-16-PT) is requested to make complete additional copies of this report for forwarding to such other agencies as may be interested.

L. V. HONSINGER
Captain, U. S. N.
Acting

DISTRIBUTION To:

CNO (OP-16-PT)	Copy Nos.	1 - 4
CNO (OP-16-PT) .... w/Enclosure B	Copy No.	5
FIAT	Copy No.	6
Office of Research and Invention	Copy No.	7
ComNavEu	Copy No.	8
ComNavEu for Admiralty	Copy No.	9
BuOrd (Re a)	Copy No.	10
BuOrd (Re 2)	Copy No.	11
BuOrd (Re 2c)	Copy No.	12
BuOrd (Pr 6)	Copy No.	13
BuOrd (Pr 6a)	Copy No.	14
NavTecMisEu (Main Files)	Copy No.	15

~~RESTRICTED~~

TECHNICAL REPORT NO. 261-45

NITROGUANIDINE - MANUFACTURE AND USE IN GERMAN PROPELLANTS AND HIGH EXPLOSIVE SHELLS

SUMMARY

This report covers three general phases of nitroguanidine; (1) Manufacture; (2) Use in propellants; and (3) Use as a high explosive. The information on manufacture was obtained mainly from Dr. Walter Schnurr of Dynamit A.G.; on nitroguanadine propellants from Dr. Schnurr and others; and on high explosives loads from Dr. Morhardt of CPVA at Danisch-Nienhof.

October 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE.

TABLE OF CONTENTS.

NITROGUANIDINE - MANUFACTURE AND USE IN GERMAN PROPELLANTS AND HIGH EXPLOSIVE SHELLS

1. Introduction

German practice for manufacture of nitroguanidine was described to us by Dr. Walter Schnurr of Dynamit A.G. at Troisdorf and later at Krumel. Essentially, it comprised reaction of dicyandiamide with ammonium nitrate solution, drying the guanidine nitrate, and rearranging this compound to nitroguanidine by treatment with either 99% nitric acid or 96-98% sulfuric acid. The importance of particle size was well recognized (See Appendix A).

Nitroguanidine was used in flashless powders for anti-air-craft guns and for cool propellants of other types. Samples of nitroguanidine powders have been shipped to Naval Powder Factory for studies of particle size, including distribution and flocculation, and for closed bomb tests to compare burning characteristics with powders under current development in the States.

The material had been studied intensively as an insensitive high explosive filler for armor piercing naval shells. Shortage even for propellant powder precluded its adoption as a load for projectiles.

2. Details

(A) Manufacture

Nitroguanidine was manufactured at Hohensaaten and, in lesser quantity, at Christianstadt. The Christianstadt equipment was removed to Aschau in Bavaria. The process as described by Dr. Schnurr involved the steps: dicyandiamide to guanidine nitrate; conversion to nitroguanidine nitrate; hydrolysis to nitroguanidine; and recrystallization to the proper particle size.

The calcium cyanmide was powdered; the excess carbide was removed by treatment with a small quantity of water; and conversion to dicyandiamide was effected by further treatment with excess water and carbon dioxide.

2. Details. (cont'd).

The wet dicyandiamide was fed with 95% ammonium nitrate solution into one end of a large drum containing a screw conveyer. The feed end of this drum was maintained at 160° C and the exit end at 190° C. The crude guanidine nitrate so obtained had a purity of about 92%. It was recrystallized from water to give 98% purity.

Rearrangement to nitroguanidine was carried out through one of two routes, nitric acid or sulfuric acid. In the first case, guanidine nitrate was treated with 99% nitric acid (100 kilos guanidine nitrate to 230-250 kilos HNO_3) to give nitroguanidine nitrate. This intermediate was hydrolyzed in 5% nitric acid to yield nitroguanidine and 20% nitric acid. Foaming in the nitroguanidine nitrate step was apt to be severe.

If sulfuric acid were available, Dr. Schnurr preferred this route for rearrangement. On the basis of nitroguanidine, 2.5 parts of 98% sulfuric acid or 2.7 parts of 96% acid were required. The reaction was carried out at an initial temperature of 25° C, rising to 45° at the end of a 10-12 minute cycle. The kettle holding a charge of 1300 kg. guanidine nitrate and 2500 kg of 98% sulfuric acid was made of V2A steel and was equipped with both cooling coils and a jacket. The cooling water had a temperature of about 9° C.

Particle size was regulated through a very careful recrystallization, outlined in detail in a translation of Dr. Schnurr's description (Appendix A).

Storage and Shipment of Nitroguanidine

Information on shipping regulations was not obtained, but it may be assumed that the storage requirements of 20% moisture applied also to shipment. Nitroguanidine was received at Duneberg in paper bags and in iron boxes. It was stored in these boxes holding 100 kilograms each and in 2000 kilogram open bins. Since nitroguanidine is substantially water-insoluble at room temperature, storage in open bins naturally led to reduction in water content. Dr. Leunig estimated the moisture had been reduced to 3-5% at the time of the bombing on 6 April 1945.

Nitroguanidine was said not to be compatible with zinc, aluminum, and iron, and these metals were avoided in storage (except for the

2. Details. (cont'd).

closed iron boxes mentioned above). Zinc forms a nitrolate on reaction with nitroguanidine; aluminum reduces the nitro group to free ammonia; and iron reduces it to nitroso. Even though non-hygroscopic, water was avoided because nitroguanidine is a good food for molds.

Explosives Hazards of Nitroguanidine

The German conclusion that nitroguanidine containing 15-20% moisture is safe to handle coincides with United States findings. On the other hand, German experience during the bombing of Duneberg indicates that material containing 3-5% moisture may detonate with terrifying results if suitably primed (in this case by a bomb estimated to be 500 kgs.) The detonation will be described in Technical Report Number 266-45 and is mentioned here only for the sake of complete information. An estimated 200 metric tons blew a crater about 200 feet in length, 150 feet in width, and 15 feet in depth (even after considerable washing and filling during the intervening three months) Adjacent buildings such as an exposed laboratory about 150 yards away were destroyed, and the face of a fire house 200 yards away was blown out completely. On the other hand, nearby magazines covered with sand, perhaps 50 yards away from the crater but whose tops were at about ground level, were damaged only to a slight extent. Appendix B contains prints to pictures illustrating this damage.

(B) Nitroguanidine Propellants

1. Advantages

The advantages claimed for nitroguanidine propellants are:

(a) Higher loading density (increase from 0.7 to 0.8 or 0.85)
(b) Lower calorific value (reflected in decreased erosion and diminished flash)
(c) Reduced burning coefficient.

The Germans set great store by the calorific value of their powders, and determined this value carefully for each powder. Research laboratories usually were equipped with one room devoted entirely to calorimeters. Each powder of whatever type was classified according to its heat of combusion as determined experimentally and their cal-

2. Details. (cont'd).

orific table apparently played an important part in the selection of powders for high velocity guns. Nitroguanidine and other coolants were used to the limit of supplies.

The following table showing the lower variations in pressure with nitroguanidine powders is of interest:

Type	Powder Temp.	Weight Charge	Velocity	Pressure
Diglykol	10° C	4.5 kg	1020 m/s	2950 atm.
Diglykol	35° C	4.5 kg	1060 m/s	3500 atm.
Nitroguanidine	10° C	5.2 kg	1020 m/s	3050 atm.
Nitroguanidine	35° C	5.2 kg	1060 m/s	3300 atm.

2. Manufacture

Manufacture of nitroguanidine propellants was carried out with surprisingly few changes from the production of "diglykol" powders. (cf. Technical Report No. 259-45) In all cases of record, the nitroguanidine was miced dry with the "paste" (nitrocellulose - DEGN blend containing up to 35% of water) and the product was subjected to no greater incorporation time during their brief gelatinization operation. No volatile solvents were used.

At Duneberg, which claimed to be the development center for new propellant compositions, an aluminum blender about 2.5 meters in length and 3 meters in diameter had been installed recently. This held a 5 ton charge of NQ (nitrogunidine) powder. The blender was made from fairly heavy aluminum plate and was fitted with outside stiffeners. Its rate of revolution was 10-12 r.p.m. Filling was done through a hopper on the deck above, and discharge on the deck housing the blender.

The blended mixture (or more often the unblended paste) was transported to the mixer house. The steel mixers were of the W.P. type similar to ours, but they had no provisions for quick opening or for vent in case of fire. However, Dr. Leuhig stated Duneberg never had had a fire in these mixers. Powders of whatever type, NQ or diglykol, were mixed for one hour in 150 kg portions. The paste, nitroguanidine if it had not been added in the blender, graphite, and stabilizer were added at the beginning of the cycle. The temperature

2. Details. (cont'd).

was maintained at 40-50° C by the circulation of water through the jacket and the bronze blades. The paste was packed in rubber lined duck bags and was aged at room temperatures for one week.

The material from the mixers was transported in trays to a roll house. The houses varied in capacity, and the rolls in size according to the year of installation. The latest type had 4 or 6 rolls per building, each in a separate room. These rolls were of steel, 1.20 meters in length and 0.35 meters in diameter, and always were driven at equal speed because of danger of fires. Differential speed rolls never were used. The knives were of bronze. The charge was 15 kg for low calorific powders such as NQ (700-800 cal./gm) Roll temperatures were maintained at 90° C for NQ powders in comparison with 70-80° C for diglykol powders. Moisture was reduced from 30-40% to 0.5% for NQ powders during the rolling operation. Each set of rolls was equipped with water deluge (usually from a tank above the rolls but occasionally from jet nozzles) and an electric eye which was supposed to function in 0.15 to 0.20 seconds.

The production of the tubular powder, which was the next step, was carried out in presses ranging in diameter from 17 cm. up to the single giant 52 cm press (See Technical Report No. 141-45 "German Fifty-Two Centimeter "Mamouth Press" for the Extrusion of Rocket Propellants".) Most if not all of the NQ powders were pressed in upright 17 cm presses (15 kg charges) of which Duneberg had a large number. A typical house held four 17 cm presses. It was built in a pagoda-like fashion with four roofs, although there were but two levels. Ample areas were given to the roof structure. The press design, which permitted full opening of the chamber just above the die, in case of sudden pressure increases, is described in Technical Reports Nos. 259-45, and 260-45. Pictures of a press house are attached in Appendix C. Perhaps because of these safety features, press buildings were erected as close to one another as 25 yards.

The finished powder was aged for at least one week before testing prior to packaging for shipment. A list of the compositions and the guns in which nitroguanidine powders were used is given, in Appendix D. This list was furnished by Dr. Leunig of Duneberg.

3. Substitutes For Nitroguanidine in Propellants

Substitutes for nitroguanidine included dicyandiamide, nitrated dicyandiamide (notoidin), melamine, and methylene urea. These are discussed by Dr. Leunig in his several summaries and are reported separately. None of them was used in the field and the only information is that available from Dr. Leunig.

C. Nitroguanidine As High Explosive

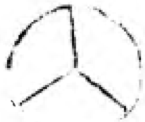
1. Advantages

The advantages claimed for nitroguanidine as a high explosive pressed charge in armor-piercing shells, as given by its chief propoenant, Dr. Erich Mohrhardt of C.P.V.A., Danisch-Nienhof, are as follows:

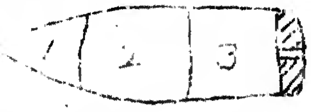
1. Insensitivity - Not one case of detonation on contact or in penetration of armor plate has been observed.
2. Fragmentation - This was somewhat better than the standard TNT results.
3. Stability on Storage - Excellent.

2. Use

Nitroguanidine was loaded in 28, 30.5, 38, and 40.6 cm shells for naval use. In all cases it was pressed to a density of 1.58 and in three or four segments of a circle:



and into two or three sections as shown:



in these rough drawings. Each portion of the nine or twelve segments was wrapped in paper, and all were loaded into the shell without subsequent consolidation. The nose position of all naval shells was (No. 1 above) said to be removable so that only one type of shell had to be stocked. The end use, whether armor piercing, high explosive, or gas, determined the composition of the nose section. The changes were made in magazines ashore, and not on shipboard.

Dependable initiation of nitroguanidine was secured by using a large booster of hexogen/wax (43-95/7-5) in the base of the shell. This was several centimeters in length and of the same diameter as the NQ charge. The insensitivity of nitroguanidine was demonstrated in firing trials. A large pile of 28 cm loaded shells were subjected to fire from 8.8 and 10.5 cm guns. No detonations were obtained, but occasional deflagrations were noted. Unconfined nitroguanidine pressed to 1.58 density did not fire when shot with their 3.7 cm gun.

Nitroguanidine could not be used for mines and torpedoes because its low heat of combustion made it less valuable for this use than other more readily available explosives.

Granular material was preferred from the standpoint of pressing. When the nitroguanidine was obtained in needles, a preliminary pressing followed by grinding was employed. This broke up the needles sufficiently so that satisfactorily density (1.58) was obtained.

Fragmentation was somewhat better than that obtained from TNT as judged by their "splinter density" test. This value was determined by firing a 10.5 cm shell statically in an area surrounded by 1 square meter paper shields. The distance in meters at which one splinter per square meter was observed is the "splinter density". Comparable values are:

Cast TNT	37-37.5 meters
Pressed TNT	30.2 meters
Pressed NQ	39.2 to 0.3 meters

D. Guanidine Nitrate.

The shortage of sulfuric acid prompted studies of guanidine nitrate in the hope this compound could be used. Apparently the study was not carried far and was limited to cast compositions for use in naval guns ashore. Guanidine nitrate and TNT mixtures tend to decompose with evolution of brown fumes at temperatures above 110° C. Hexogen accelerates this decomposition and ammonium nitrate retards it.

2. Details (cont'd).

Below 100° C, the mixtures were said to be as stable. A typical composition was given:

Hexogen	5 %
Ethylene diamine dinitrate	10
TNT	10
Guanidine Nitrate	10
Ammonium Nitrate	55
Potassium Nitrate	6
Calcium Nitrate	4
Emulsifier*	0.2
Pouring Temperature	80°C
Velocity	6250 m/s
Oxygen Bal.	+ 1.1
Density	1.59
Lead Block	357 cc

* I.G. Vultamol, sodium naphthalene sulfanate

This amatol-like mixture contained a surprisingly large number of materials, but the guanidine nitrate content was so low (10%) as not to influence seriously the properties.

A nitroguanidine composition pourable at 80° C was given as follows:

TNT	40%
PETN or Hexogen	10
Nitroguanidine	20
Aluminum	30

A small portion of oxalic or benzoic acid was used, especially if alkalinity were noted.

Specifications for purity of guanidine nitrate were set up:

Melamine	less than 0.4%
Ammonium nitrate	0.2 - 0.5
Water insoluble	0.5 - 0.9
Ash	0.01 - 0.04
Reaction	Neutral
Melting Point	211 - 213°C

3. Appendices.

Appendix A.

Recrystallization of Crude Nitroguanidine

Translation of Dr. Walther Schnurr's Description.
Duneberg, 12 July 1945.

The following apparatus was used in the nitroguanidine plant at Hohensaaten for purification of the crude salt:

(1) Disolving the crude salt: Two cylindrical vessels made of V2A, each with a capacity of 12 cbm, equipped with stirrers and heating coils. Each vessel had a bottom draw-off valve protected by a small screen to remove coarse impurities.

(2) Filtration. One Scheibler-filter for each solvent vessel. The filter contained 14 frames which were covered with filter bags of linen cloth. Total filter surface ca. 25 sqm.

(3) Crystallization. Two vacuum boilers which were connected to the Scheibler-filter by a pipe line 10 cm. in diameter, made of V2A. These vacuum vessels were V2A plated boilers each with a capacity of 15 cbm and equipped with a stable blade agitator. On the cover of these vacuum vessels there were attachments for: inflow of nitroguanidin solution and water, compressed air measuring instruments, and compressed air for discharge of the contents.

(4) Centrifuge. Three suspended drive centrifuges as are used in nitrocellulose manufacture. These centrifuges contained filter cloth inlays of cotton and cotton wool respectively. Over this cloth inlay there was a sieve of rust-proof steel to protect the cloth from damage at the time of discharge.

(5) Supply vessel of V2A for mother liquor, wash water, aqueous ammonia, etc.
Manufacture of G-Salt for propellants. A mixture of 8 cb.m. mother liquor and 4 cb.m. water was introduced into the solution vessel first a "receiver". This liquid was heated to 70° C., and ca. 1000 kg. moist crude nitroguanidine containing ca. 25% H_2O was added through a funnel. This charge

3. Appendices (cont'd).

was heated to 100° with rapid agitation to effect solution, after which it was adjusted to PH = 7 with concentrated ammonia using brom thymolblue as the indicator. The neutral or slightly alkaline nitroguanidine solution was held at high temperature for as short a time as possible to minimize losses through hydrolysis. The hot solution was pumped in a jacket-heated V2A line of 150 mm diameter by means of a centrifugal pump (capacity, 60 cb.m./b with a lift of 20 m), through the Scheibler-filter, and into the vacuum vessel for crystallization. For this purpose first 3 cbm of hot, neutral, filtered nitroguanidine solution were pumped without vacuum into the boiler to control the formation of the crystal nuclei; then the remainder of the solution was added at a 560 mm absolute vacuum. As soon as the solvent vessel had been emptied into the vacuum vessel, full vacuum was applied and the solution cooled to at least 45°. Crystallization took place under constant stirring. After breaking vacuum, the crystal suspension was forced by compressed air directly to the centrifuges. The mother liquor was removed, the cake washed with water for a minute, and centrifuged again. The 40 - 44° C. water mother liquor and the wash water from the centrifuges discharged into mother liquor vats provided for this purpose. The mother liquor was returned to the process as mentioned earlier in this manuscript. The remainder, amounting to ca. 3 cbm, was worked up practically without loss through use as dilution water in crude salt production.

In this manner piling up of by-products in the crystallization liquors was avoided. Nevertheless, consideration was given to occasional discharge of all the mother liquor into the crude salt production process and to crystallization with fresh water, in order further to avoid piling up of by products.

In addition, once daily a wash water charge was sent through the whole system in order to remove crystal deposits and coatings in containers, "pipe" lines, and valves to keep the whole crystallization apparatus clean. At the same time, a change of filter cloth in the Scheibler-filter was made.

The finished product was removed from the centrifuges with an average water content of 6.5% transported in aluminum carts, and emptied into containers built of masonry lined with tile. Here several charges (about 1000 kg.) were thoroughly mixed and, after a sample had been taken, poured into vats.

In this way a uniform product was obtained with a relatively high bulk density. The maintenance of exact concentrations and absolutely constant crystallization conditions were indispensable for uniformity of product. The slightest deviation from these factors led to great changes in the crystal form.

On the other hand, it was possible to produce various crystal forms by suitable changes in the conditions of concentration, cooling, or crystallization, respectively.

For the production of heavy G-Salt. The same apparances generally was used as described above for the production of nitroguanidine for powder. 1000 kg. of crude salt obtained on dehydration with an average moisture content of ca. 25% H_2O were dissolved in 11 cbm of a solution mixture consisting of water and mother liquor and then heated. The solution heated to 100° was neutralized with ammoniacal water to a PH value of 7.

A tylose solution (consisting of 500 g dry tylose (methylcellulose) SL 25 in water) was added to this G-salt solution and stirred well. The G-salt solution was filtered through a Scheibler-filter and within 2 hours cooled to 45° C. under vacuum with uniform slow stirring. At the beginning of the cooling process the temperature was lowered very slowly because within the ranges of 100 - 80° C. the main stock of the nitroguanidine precipitates and the character of the crystal form is determined by the rapidity of this operation.

The G-Salt suspension thus obtained was separated from the mother liquor by means of centrifuges.

In order to obtain a material with especially high bulk

2. Appendices. (cont'd).

density it was advantageous to sieve the material after drying.

Signed by:

Dr. Walther Schnurr.

Appendix B.

View of NQ Crater Showing Adjacent
Hydrogen Peroxide Vault.

Appendix C.

Views of Press House (Duneborg)

Appendix C. (cont'd).

View of Press House (Duneberg)

Designation using German Gu in place of NQ	Use by: H = Army M = Navy L = Air Corps	Composition	Percent	Heat of Combustion cal./gm. Observed	Heat of Combustion cal./gm. Calculated	Calculated f-value	Gas Volume cm^3/kg	Explosion Temperature °C	Guns whic
Gu P - AO. - AO.25 - AO.5 - Al. - Al.2	H	DEGN	31.23	930	830	10,820	993	2880	1.F. 15.0 42/2 10.5 21.0
		NC (12%, N)	38.17						
		NQ	30.00						
		Akardite	0.50						
		Graphite	0.10						
		K_2SO_4	0.25 - 1.2						
R.P. 39	M	DEGN	21.76	830	713	9,870	1023	2550	
		NC (12.2% N)	35.49						
		NQ	40.00						
		Akardite	0.50						
		Ethyl phenyl urethane	0.70						
		MgO	0.25						
		Graphite	0.10						
		K_2SO_4	0.50						
		Diphenyl urethane	0.70						
u R.P. - 7.5	L H	DEGN	18.30	750	537	8400	1100	2020	8.8
		NC (12% N)	42.70						
		NQ	30.00						
		Diphenyl Urethane	5.00						
		Ethyl phenyl urethane	3.75						
		MgO	0.15						
		Graphite	0.10						
R.P. - 8	H	DEGN	20.62	810	736	10,015	1007	2630	
		NC (12% N)	48.13						
		NQ	30.00						
		Ethyl phenyl urethane	1.00						
		MgO	0.15						
		Graphite	0.10						
R.P. - KN	L	DEGN	16.95	720	518	8100	1074	1995	8.8 c
		NC (12% N)	39.55						
		NQ	30.00						
		Diphenyl urethane	4.25						
		Ethyl phenyl urethane	5.00						
		MgO	0.15						
		Graphite	0.10						
		KNO_3	4.00						
P. - GO - - GO.5 - - G1 -	H	DEGN	18.30	730	531	8355	1102	2005	12.8 8.8 cm
		NC (12% N)	42.70						
		NQ	30.00						
		Diphenyl urethane	3.75						
		Ethyl phenyl urethane	4.50						
		Akardite	0.50						
		MgO	0.15						
		Graphite	0.10						
		K_2SO_4	0.5 - 1.0						
P.P. - G5 -	H	DEGN	18.23	730	476	8600	1051	1890	21.0 c 38.0 c 40.6 c
		NC (12% N)	42.52						
		NQ	25.00						
		Dephenyl urethane	4.50						
		Ethyl phenyl urethane	4.50						
		MgO	0.15						
		Graphite	0.10						
		K_2SO_4	5.00						

~~RESTRICTED~~

Prepared by:

Lt. Comdr. C.H. BROOKS, USNR.

Lt. G.H. NEFF, USNR.

Lt. T.L. MILLER, USNR.

J.B. CASTNER, Technician.

Dr. W.E. LAWSON, Technician.