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CONVERSION OF PROPELLANT GRADE PICRITE TO SPHERICAL NITROGUANIDINE

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R J SPEAR L D REDMAN AND R BARROW

MRL-TR-91-33

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Conversion of Propellant Grade Picrite to Spherical Nitroguanidine, an Insensitive Filler for Melt-Cast TNT Formulations

**Robert J. Spear, Lance D. Redman
and Russell Barrow***

MRL Technical Report
MRL-TR-91-33

Abstract

The preparation of spherical nitroguanidine (SNQ) from Australian propellant grade picrite (NQ) has been investigated. A method based upon N-methylpyrrolidone (NMP) and acetone as solvent/non-solvent has been found to give a good quality SNQ product from a variety of picrite batches. Larger spheres can be grown under these conditions by controlled seeding. Attempts to use recycled NMP and acetone gave an unsatisfactory product in general. Use of aqueous based systems gave poor product. Particle size, bulk density and hazard properties are determined for a number of batches. Recommendations on future research to evaluate SNQ formulations as insensitive main charge explosives are outlined.

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* *Vacation scholar at MRL, November 1987 to February 1988*

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Lance Redman attended Royal Melbourne Institute of Technology, graduating with a Diploma of Applied Chemistry in 1971. He worked in the laboratorics at Carlton and United Breweries for two years before joining MRL in 1970. At MRL he has gained a wide range of experience in handling explosive materials both primaries, secondaries and pyrotechnics. He is currently working on high velocity impact sensitivity and laser ignition of pyrotechnic compositions.

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Russell Barrow was a vacation scholar at MRL over the period November 1987 – February 1988. Russell returned to University of Melbourne in 1988 where he completed his BSc(Hons) in organic chemistry and subsequently commenced a PhD on natural products in marine organisms.

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Conversion of Propellant Grade Picrite to Spherical Nitroguanidine, an Insensitive Filler for Melt-Cast TNT Formulations

1. Introduction

Shell and bomb fillings for Australian production and Service use are almost exclusively based on TNT and filled using melt-cast production methods. Two typical fillings are Composition B (TNT/RDX/beeswax 40:60:1) and H-6 (TNT/RDX/Al/D2 wax/$CaCl_2$ 30:45:20:5:0.5). High production rate shell and bomb fillings in UK and US production are also largely TNT based, although there is a continuing trend to replacement by polymer bonded explosives (PBXs). PBX-filled stores exhibit significantly lower vulnerability to stimuli such as cook-off (fuel-fire), bullet/fragment impact and mechanical drop. A major technical limitation of PBXs is that the high production rates which would be required in an emergency are not yet available, although continuous processing methods which would overcome the problems are the focus of much R & D effort throughout the Western world.

Due to this technical limitation, and also taking into account Australia's major investment in melt-cast production plant, continued reliance on TNT-based formulations is inevitable for the foreseeable future. Exceptions could include lower production rate items such as sea mines or missile warheads, or specific munitions where reduced vulnerability is essential, such as naval shell warheads. Reductions in the vulnerability of munitions filled with Composition B or H-6 can potentially be achieved by replacement of RDX by a less sensitive but still high performing explosive filler. At MRL we are currently undertaking a program to examine a number of such fillers. In this report we describe one study, that on spherical nitroguanidine (SNQ).

2. Nitroguanidine (NQ, Picrite)

NQ is cheap and easy to manufacture, has very low sensitiveness to impact, and a relatively high crystal density and detonation velocity. Data on NQ from various sources [1-4] are compared with data for TNT and RDX in Table 1. The principal use of NQ in western countries is in triple base propellants. These are manufactured for Australia by Australian Defence Industries at their Mulwala Facility.

Table 1: *A Comparison of Published [1-4] Material and Explosive Properties of Nitroguanidine (NQ), TNT and RDX*

Property	NQ	TNT	RDX
Molecular weight	104 1	227.1	221.1
Density, Mg/m^3	1.775	1.654	1.806
Melting point, °C	245-257 (decomp)	80 9	204-5 (decomp.)
Heat of formation, kJ/mole	- 84.89	- 50.2	+ 61.55
Heat of combustion, kJ/mole	- 880 3	- 3419.2	- 2099.5
Impact sensitiveness:			
Type 12 (2.5 kg), cm	> 320	212, 148	22, 28
(5 kg), cm	> 177	80	28
Type 12B (2.5 kg), cm	> 320	approx. 100	41, 32
Shock sensitivity:			
LASL LSGT, mm at [density, Mg/m^3]	5.00 [1.609] No Go [1.715]	52.53 [1.595, pressed] 28.30 [1.615, cast]	61.82 [1.750]
Detonation velocity, km/s [density, Mg/m^3]	8 563 [1.775] 7.65 [1.55] (1.44 + 4 015 ρ)	6.999 [1.62] (1.873 + 3 187 ρ)	8.800 [1 806] 8 639 [1.767] (2.66 + 3.40 ρ)
Detonation pressure, GPa [density, Mg/m^3]	25.8 [1.704][a] 20 55 [1.55][b]	18.91 [1.637]	33.79 [1.767]

[a] Data for NQ/Estane 95 5, detonation velocity 8.28 km/s.

[b] Calculated [4].

Despite the apparently favourable properties, NQ has found little use in explosive fillings; the only documented use is by Germany in WWI and WWII [3]. One major reason is the poor physical form of NQ, which typically crystallizes as matted agglomerates of long needles, often hollow, with bulk densities below 0.25 Mg/m^3. It is very difficult to compact this material above 80% theoretical maximum density (TMD) [5], even with incorporation of a binder, while addition of as little as 10% w/w into molten TNT results in an unpourable suspension [5].

In 1947 Pritchard and Wright [6] found that crystallization of low bulk density NQ from a variety of solvent combinations gave more equant crystals with a bulk density approaching 1.0 Mg/m^3. This material, commonly called high bulk density NQ (HDNQ)[1], can also be prepared by aqueous crystallization using a variety of crystal modifiers such as methyl cellulose [8], mannan [9], PVA [10], gelatin [11] and some benzaldehyde derivatives [12, 13]. The levels that can be incorporated into molten TNT are substantially better than low density NQ; compositions containing up to 40% w/w have been prepared, however the increase of HDNQ content above 40% w/w rapidly leads to unprocessible suspensions [5]. Considerable effort is still being devoted in the US to improving the physical properties of HDNQ. This is expected to lead to increased incorporation into TNT, and more easily processed propellants [7].

A German method for preparing NQ in a spherical form (SNQ) possessing high bulk (pour) density of 0.9 to 1.1 Mg/m^3 was reported in 1981 [14]. Existing and continuing patent action on these processes has been undertaken [15, 16] and material can be purchased in small quantities from ICT in Germany. SNQ has the advantage both of high bulk density as well as improved packing achieved by use of spherical particles in suitable particle size blends [17]. These favourable properties should permit an increase of NQ/TNT ratios over those observed previously with HDNQ [5]. Schedlbauer [18] and Volk [19] have reported processible SNQ/TNT formulations with ratios in excess of 60:40 using selected particle size blend ratios of SNQ.

The aim of the work reported here was to prepare and characterize SNQ from propellant grade NQ used in Australian production of triple-base propellants. Further assessment, including processibility of molten TNT/SNQ suspensions and performance of cast charges, is being carried out in a follow-on study, using both locally produced SNQ and material purchased from ICT.

3. *Preparation of Spherical NQ (SNQ)*

The technical description of the German process for SNQ [14, 15] is very broad and suggests a variety of solvent combinations, both aqueous and non-aqueous, together with unspecified crystal modifiers, which can produce material of the desired form. More detailed information concerning non-aqueous methods for preparing spherical NQ were obtained during visits by one of us (RJS) to Los Alamos National Laboratory in 1986 and by Dr I.J. Dagley to ICT in 1987. This information served as the starting point for one aspect of our study. After this work was completed, both a conference paper [20] and a US patent [21] for producing SNQ were published. The method described in these publications [20, 21] was very similar to the optimum method which we developed.

The formation of spherical particles or balls only occurs for very polar organic molecules or inorganic salts; in the latter case many naturally occurring examples are found, e.g. calcium carbonate. Most high explosives are not sufficiently polar; RDX does not form spheres [22].

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[1] This is sometimes referred to as spheroidal NQ in US reports [7].

Both the German ICT [22] and US [20] experience is that a number of properties of the picrite raw material can influence production of spheres. Best results are obtained for neutral (pH 7) picrite, otherwise needles and other particle forms can be produced in competing processes. Each new batch of picrite must first be screened to ensure suitability for production of spheres. A number of additives have been evaluated without achieving consistently good results. The US patent [21] describes the use of nickel salts as additives and apparently some picrite batches will not form SNQ without them [20]; it is not known whether these were screened by ICT.

An aqueous process is preferable for large scale production since current occupational health and safety concerns place restrictions on use of solvents, and these restrictions are likely to become more stringent in the future. This was given as the principal reason for continued development programs for HDNQ in the US, while the Germans have also been very actively seeking alternative aqueous processes to their solvent based methods [23, 24]. We also extensively investigated the preparation of SNQ using aqueous systems during this study.

3.1 Materials

3.1.1 Nitroguanidine

Information from both US and German sources was that no "general" method would be successful for all production batches of propellant grade NQ, even if they originated from the same source. We accordingly chose to investigate as wide a range of NQ batches as possible and consulted Explosives Factory Maribyrnong (EFM) production staff prior to selection. The two main sources of NQ for Australian production are Germany and the UK. Samples of these materials were obtained from EFM. In addition small quantities of Canadian NQ were located at MRL. Details of all NQ batches used are given below in Table 2.

Table 2: *NQ Batches Used to Prepare Spherical Material*

Batch	Source
Lot 6	Nigu Chemie, Germany. Reserve stock obtained via EFM
731A	All batches 731A-832 ex ROF Bishopton, UK, obtained via EFM
732	
791	
793	
811	
812	
831	
832	
X/12/40 CRC 14 (Class 3, Div. 2)	Welland Picrite Inc., Canada. Stock held at MRL
HC 6839	Welland Picrite Inc., Canada. Stock held at MRL

Australia has never produced NQ on a commercial scale although a number of pilot batches were made at EFM over 20 years ago using the Canadian process [25].

3.1.2 Solvents

Solvents used for small scale preparations (total volume < 2 L) were laboratory grade except dimethylsulfoxide (DMSO), N-methylpyrrolidone (NMP) and ethylene glycol (EG) which were AR grade. Larger scale preparations were carried out with industrial grade solvent used without further purification. Water was distilled.

3.1.3 Surfactants/Additives

The additives investigated during the course of the study are listed below. Most are surfactants. All were obtained either as aqueous solutions or solids and were used as received.

Cetyltrimethylammonium bromide, methyl cellulose and Aerosol OT (all BDH), Mowiol 4-88 (Hoechst), Orotan 960 and 731-SD and Lomar D (Rohm and Haas), phospholan PDB-3 and Nopcote RGX-2 (Diamond Shamrock), Empilan AQ100 (Albright and Wilson) and gelatine (Ajax). Tween and dextrin were commercial samples of unknown specification.

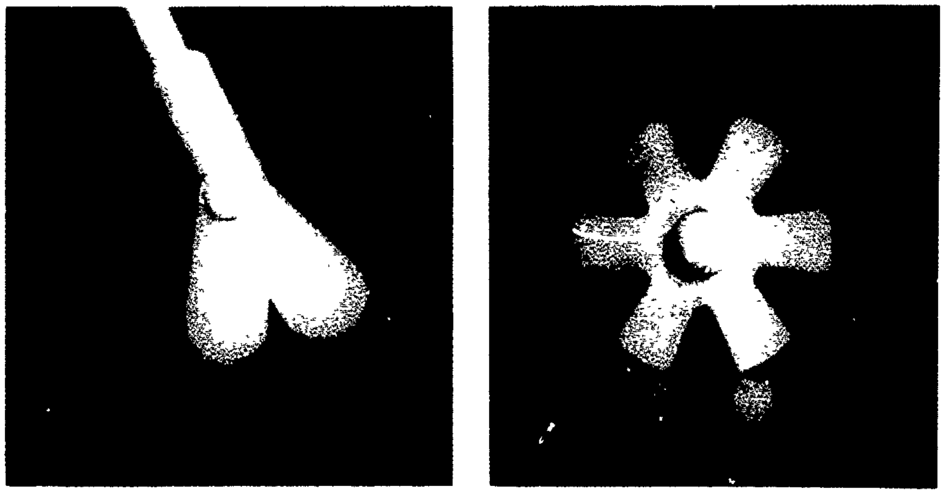
3.2 Apparatus

3.2.1 Batches up to 50 g

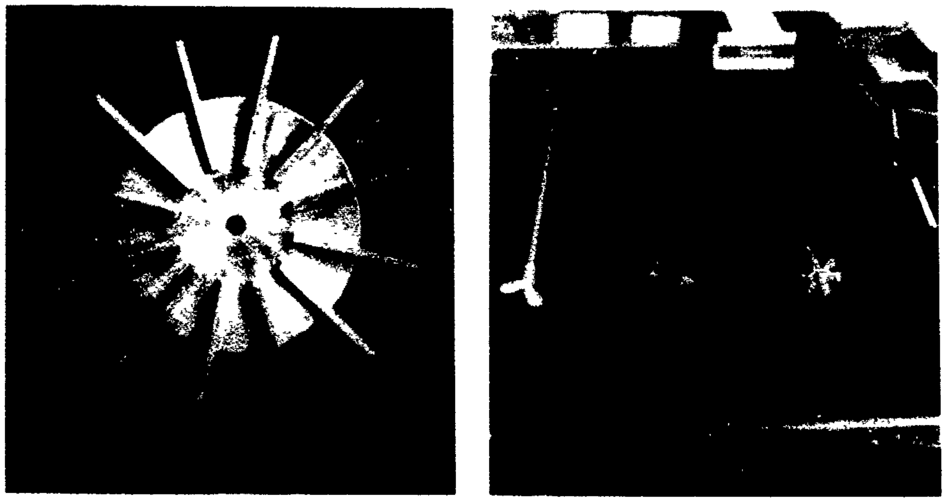
Batches ranging from 5 g to 50 g were prepared either in a beaker or Erlenmeyer flask. Depending upon NQ mass and total volume, these ranged in volume from 500 mL to 5 L. Stirring was effected using an air driven overhead motor with three types of stirrer as depicted in Figure 1; a collapsible paddle (Fig. 1a), a propellor (1b) and a bladed impellor (1c). Throughout the text these will be referred to as stirrers 1a, b and c respectively. The top of the beaker or flask was covered by aluminium foil to inhibit evaporative loss of solvent. Heating was effected by a water bath on a hot plate, cooling involved use of an ice bath.

3.2.2 Batches up to 200 g

Larger batches up to 200 g were prepared using a jacketted 10 L stainless steel pan equipped with an air driven paddle stirrer and provision for heating and cooling (Fig. 2). An aluminium foil cover was also used to minimize evaporative loss of solvent.



(a) 55 mm wide (b) 45 mm



(c) 67 mm (d)

Figure 1: Stirrers used for small scale batches of SNQ up to 50 g size. Dimensions of the stirrers can be gauged from (d) by comparison with the pen on the right hand side centre of the frame.

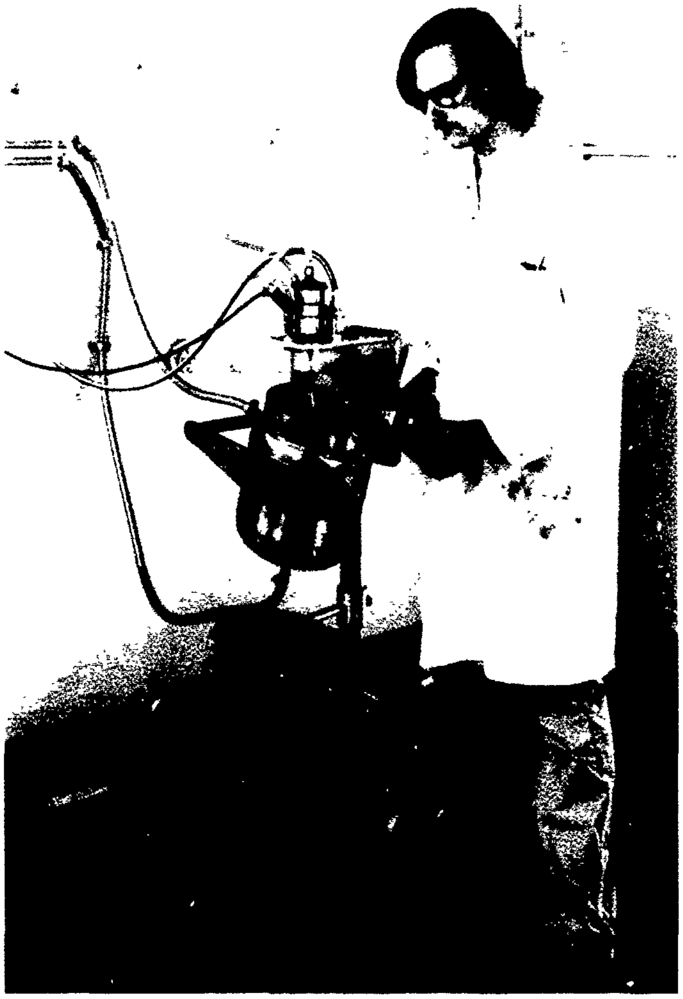


Figure 2: The 10 L stainless steel reaction vessel used for 200 g SNQ batches.

3.3 Methods of Recrystallization

The methods of recrystallization used throughout the study fell into two broad types.

Method A:

NQ was dissolved by heating to 70 to 80°C in a solvent in which it was readily soluble. The solvents were either DMSO, NMP or dimethylformamide (DMF), or admixtures, and resulting solutions were near saturation at 70°C. The hot solution was then added, while maintaining vigorous stirring, to a larger volume of either pure acetone or admixtures with ethanol, methanol or water. The best products were obtained when the acetone solutions were maintained at 10 to 30°C. Additives to induce crystal modification were dissolved in either solution. The SNQ was recovered by gravity filtration.

Method B:

NQ was added to a solvent or mixture of solvents in which it was only moderately soluble; this may also contain additives. Stirring was continued while the temperature was held at 90 to 95°C. When the NQ had completely dissolved (additional solvent may need to be added to achieve this) the solution was slowly cooled while maintaining stirring. Solvents used were water with methanol, ethanol, acetone or ethylene glycol, with smaller quantities of DMSO, NMP or DMF also added in some experiments. Surfactant additives were also added to the solvent solution in most cases.

3.4 Product Assessment and Characterization

Particle Size Determination

The dried SNQ was passed through a nest of Endecott 20 cm diameter sieves of the following aperture sizes; 2.36 mm, 1.70 mm, 1.00 mm, 600 µm, 300 µm, 150 µm, 106 µm, 75 µm, 45 µm. Each batch was sieved by gentle shaking and brushing for a total of 10 to 15 minutes. Material retained on each sieve was removed and weighed.

Microscopy

Optical microscopy was performed using a Leitz Ortholux microscope. Photomicrographs were taken with a Leitz Orthomat 35 mm automatic camera on polaroid film type 667. Magnification ranged up to X42.

Scanning Electron Microscopy (SEM)

SEM was performed using a Cambridge Instruments Model S250 Mk II scanning electron microscope with a tungsten electron gun. The instrument was operated at 20 kV in the secondary electron mode. Samples were mounted on a stub coated with a conducting film of gold. The micrographs were normally obtained for tilt angles of 20 to 30 degrees.

Bulk Density

An accurate mass, M_1, of SNQ was weighed into a graduated measuring cylinder which was placed on a commercial vibratory polisher. The SNQ was allowed to settle under vibration to a minimum volume V_1.

Mixed or bimodal packing was achieved as above for M_1, then an amount of a finer SNQ was added till just in excess. This was subjected to vibration, then further SNQ was added in portions till no further settling of the fine spheres into the coarse was observed. The total mass of fine SNQ was M_2, minimum volume V_2

$$\begin{aligned}\text{Bulk density} &= M_1/V_1 \text{ for a single batch}\\ &= (M_1 + M_2)/V_2 \text{ for a mixed batch.}\end{aligned}$$

Vacuum Thermal Stability [26]

The test procedure consisted of placing duplicate 5 g samples in glass sample tubes, attaching to a mercury filled manometer and evacuating. The sample tubes were then placed in a heated bath at 120°C, and a 1.5 h period allowed for temperature equilibrium. The volume of gas evolved was then monitored for 40 h. The quoted result is gas evolved in mL/5 g at 120°C for 40 h and is the average of duplicate samples.

Rotter Impact Sensitiveness [27, 28]

Impact sensitiveness was determined using a Rotter apparatus [27]. Each sample of about 30 mg confined in a brass cap fitted over a polished steel anvil was impacted by a 5 kg weight falling from a preset height. Ignition was defined as either > 1 mL gas evolution or more usually > 0.5 mL accompanied by smoke as evidence of combustion [28]. The resulting Figure of Insensitiveness (F of I) is calculated relative to RDX Grade F = 80 and is rounded to the nearest 5 units. Gas evolution represents the average for all ignitions.

4. Results and Discussion

4.1 Initial Experiments

Experiments were commenced by dissolving NQ (up to 5 g) in a solvent in which it was reasonably soluble at 75 to 90°C; in the following text this will be referred to as the "solvent". In general this was NMP but a number of others were investigated. This solution was then added to a larger volume of a second solvent in which NQ had low solubility; in the following text this will be referred to as the "non-solvent". The non-solvent was usually acetone at either ambient or sub-ambient temperature, stirred using a magnetic stirrer.

It was soon found that the rate of addition of the NQ/solvent solution was unimportant since on most occasions precipitation did not occur till after complete addition. It was therefore decided that the NQ solution would be rapidly added by pouring in all future experiments.

Although a few spheres usually formed under many conditions, most if not all of the recovered NQ consisted of agglomerates. The possibility that the magnetic stirrer bar was either disrupting production of spheres or causing their breakup was investigated by substituting a stirrer driven by an overhead electric motor. Two designs of stirrer were tried, 1a and 1b (Fig. 1) and production of spheres was greatly enhanced under these modified conditions. It was also observed that provided efficient stirring of the solution was maintained without excessive agitation, neither the speed nor whether stirrer 1a or 1b was used had a large effect on SNQ production.

The lack of dependence of SNQ production on both stirrer speed or design can be seen in the following results but is not further commented upon in any detail.

4.2 Non-Aqueous Solvent/Non-Solvent Methods

4.2.1 Small Scale (5 g) NMP/Acetone Preparations

The large number of experiments conducted are listed in chronological order in Table 3. To aid appreciation of the result/comment section, examples of good spheres, irregular or rough spheres, agglomerates shaped like raspberries and needle agglomerates are shown in Figures 3a, b and c and d respectively. Other comments can be inferred from the types depicted.

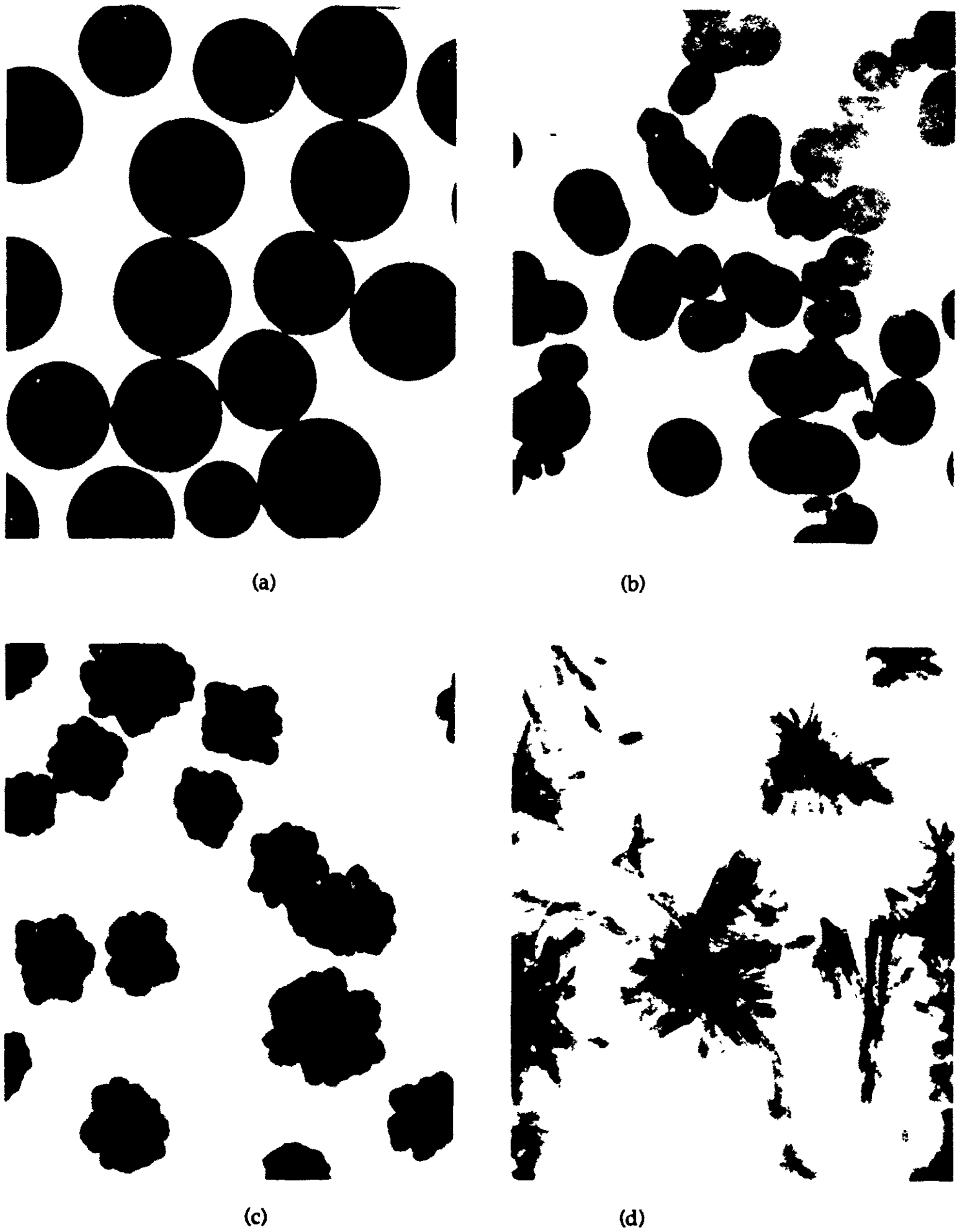


Figure 3: Representative SNQ products showing a range of crystal habits obtained. (a) good spheres (batch 198/87); (b) irregular spheres (batch 113/87); (c) raspberry shaped agglomerates (batch 81/87); (d) needle agglomerates (batch 105/87).

Table 3: Small Scale (5 g) Batches of SNQ Prepared Using NMP/Acetone Plus Additives

Batch No.	Picrite Batch[a]	NMP Vol (mL)/ Temp (°C)/Stirrer[b]	Acetone Vol (mL)/ Temp (°C)/Additive	Result/Comment
42/87	832	25/80/B	200/25	Stir 1 h in ice bath. Spheres
43/87	832	25/80/B	200/25/Tween[c]	No product until cooled in ice bath. Larger spheres than 42/87
44/87	X/12/40	25/80/B	200/25	Product forms after 5 min. Low density spheres
45/87	X/12/40	25/80/B	200/25/Tween[c]	
46/87	Lot 6	25/80/B	200/25	Range of small spheres
47/87	Lot 6	25/80/B	200/25/Tween[c]	Small yield of large spheres. Finer material appeared overnight
48/87	811	25/80/B	200/25	
49/87	811	25/80/A	200/25/Tween[c]	Spheres plus fines
50/87	812	25/80/B	200/25	Spheres plus fines
51/87	812	25/80/A	200/25/Tween[c]	Spheres plus fines
52/87	831	25/80/A	200/25	Spheres
53/87	831	25/80/B	200/25/Tween[c]	Larger spheres (3-4 mm), lower yield than 52/87
54/87	732	25/80/A	200/25	Small spheres
55/87	732	25/80/B	200/25	Large spheres plus fine material
56/87	791	25/80/A	200/25	Small spheres
57/87	791	25/80/A	200/25/Tween[c]	Larger spheres than 56/87
58/87	793	25/80/B	200/30	Large spheres
59/87	793	25/80/B	200/0	Large spheres
60/87	791	25/80/A	200/25/phos[d]	No product after 1.3 h, precipitated after 20 mL ethanol added 61/87
61/87	793	22[e]/80/B	200/25	Large spheres
62/87	791	22[e]/80/A	200/25/phos[d]	Spheres
63/87	793	22[e]/80/B	200/25	Large spheres, low yield
64/87	812	25/80/A	200/30	Small spheres plus fines
65/87	812	25/80/B	200/300/gel[f]	Large spheres
76/87	832	25/80/B	200/30	Slowest stirrer speed (180 r/min); no spheres, hemispheres on walls and stirrer
77/87	832	25/80/B	200/30	Fastest stirrer speed (600 r/min); mixed product of fines and spheres

	Picrite Batch[a]	NMP Vol (mL)/ Temp (°C)/Stirrer[b]	Acetone Vol (mL)/ Temp (°C)/Additive	Result/Comment
78/87	832	25/80/A	200/30	600 r/min, large spheres
79/87	832	25/80/A	200/30	320 r/min, spheres smaller than 78/87
80/87	832	25/80/A	200/17	320 r/min, fines and spheres
101/87	X/12/40	25/80/A	200/20/Mow[g]	320 r/min, pincushion spheres plus agglomerates
149/87	HC6839	25[h]/75/A	200/30	Low density spheres
151/87	HC6839	25/75/A	200/30	Low density spheres
158/87	731A	25/75	160/32	Large spheres
160/87	Lot 6	24[i]/75	160/22	Seeded with 1 g 156/87, irregular spheres
161/87	Lot 6	24[i]/75	160/20	Large spheres
178/87	Lot 6	25/75/A	200/22	Fines
180/87	Lot 6	25/75/A	200/23	Small spheres plus fines
181/87	Lot 6	15/75/A	200/22	Small raspberries
182/87	Lot 6	20/75/A	200/23/Tween[c]	Small spheres
183/87	Lot 6	20[l]/75/A	200/38	Spheres larger than 182/87
184/87	Lot 6	20/75[j]	200/53	Medium to large raspberries
185/87	Lot 6	25/75	200/25	Very fine spheres and agglomerates
186/87	Lot	20/75/Tween[k]	200/47	Medium large spheres and raspberries
187/87	Lot 6	20/75/Tween[k]	100/49	Medium large spheres
188/87	Lot 6	20/75/Tween[k]	50/45	No product after 1 h. Add extra 25 mL acetone gave fines
189/87	Lot 6	20/75/Tween[k]	300/47	Large spheres
190/87	811	20/75/Tween[k]	300/47	Medium large spheres and raspberries
191/87	Lot 6	20/75/Tween[k]	300/50	Large irregular spheres
198/87	Lot 6	20/75/Tween[k]	200/1-2	Medium spheres
200/87	Lot 6	20/75	200/-15	Small spheres plus fines

a Refer to Table 2
b A is stirrer depicted in Figure 1a, B that in Figure 1b
c 3 drops added to acetone
d 3 drops of Phospholan PDB-3 added
e 3 mL of DMSO added to NMP
f 0.2 g gelatin added to acetone
g 5 mL of 1% Mowiol 4-88 added
h Industrial grade NMP. All other entries refer to laboratory grade
i 1 mL of DMSO added to NMP
j Stirrer type was not noted for this and following batches, as well as 158/87 and 161/87
k 3 drops of Tween added to NMP, not acetone as previous entries
l 6 drops of Tween added

In general the method produced spherical particles in yield of about 3.4 g (65 to 70% recovery). No attempt was made to optimize this. A number of variables influence the quality of the spheres:

(i) While spheres could be produced from all picrite batches used, the X/12/40 and HC6839 batches tended to give poorer products than the others.

(ii) The different stirrer types had little effect, as noted in the previous section, neither did stirring rate.

(iii) Temperature had quite a marked effect; five results are listed in Table 4. The highest quality spheres were formed at temperatures lower than ambient. These spheres were typically of narrow particle size range and below 300 µm. Increasing the acetone temperature gave larger spheres but the surface quality and sphericity decreased. If temperatures were reduced to - 15°C crystallization was too rapid and needle agglomerates were formed in a competing process.

(iv) A range of surfactants were tested in initial experiments. Tween had the most consistent influence and was the additive most used in the 5 g batches. Although not a strong effect, the tendency was for larger, higher quality spheres to be formed in the presence of Tween. It is suggested that the surfactant held up nucleation, leading to formation of fewer, larger particles.

(v) Replacement of 1 to 3 mL (out of 25) of NMP by DMSO also resulted in larger spheres but recovered yields were lower.

(vi) Reduction in the volume of NMP to 20 mL was achievable but further reduction to 15 mL compromised product quality. Reduction in acetone volume below 200 mL led to reduced yield.

Table 4: The Effect of Acetone Temperature on SNQ Prepared from NMP/Acetone

Batch No.	Temperature (°C)		SNQ Characteristics
	NMP	Acetone	
194/87	75	49	Spherical particles with rough surfaces, range 1.0 - 1.7 mm
182/87	75	23	Spherical particles, size range 150-300 µm, all had rough surfaces
176/87	65	23	Spherical particles, size range 150-300 µm, all had rough surfaces
198/87	75	1-2	Highly spherical smooth surfaced spheres, mostly 150-300 µm size
200/87	75	-15	Highly spherical smooth spheres accompanied by needle agglomerates. All material had particle size < 106 µm

4.2.2 *Small Scale Preparation Using Other Solvent Combinations*

A large number of experiments were carried out; these are listed in chronological order in Table 5. The experiments examined part replacement of acetone by ethanol, and replacement of NMP by DMSO, DMF and ethylene glycol (EG). A single experiment was attempted using pyridine (batch 197/87) but NMP had to be added to achieve the desired solubility level.

In general the results are inferior to those listed in Table 3. Trends observed are summarized below:

(i) DMSO gave poor results except when ice cooling and seeding were employed (see final entry, Table 3).

(ii) The main difficulty with EG was dissolving the picrite; this required larger volumes of solvent and higher temperatures. In one experiment the picrite was observed to liberate ammonia, indicating thermal decomposition had commenced. Needles or low density spheres were the predominant product types observed.

(iii) DMF/acetone tended to give needles or raspberries rather than spheres.

(iv) Replacement of acetone by ethanol did not produce any beneficial effect.

4.2.3 *Large Scale Preparations*

On the basis of the small scale preparations, scale-up batches to 50 g were prepared using picrite/NMP/acetone in the ratio 5:25:200. 200 g batches used ratios of 5:25:150, i.e. reduced acetone level, while later 50 and 100 g batches used ratios of 5:20:200, i.e. reduced NMP. Tween was added to most batches. The complete experiments are listed in Table 6.

The procedure scaled up well from the 5 g batches and both product quality and yield were maintained. The spheres can be readily separated from any needles or fine material by sieving; the latter can then be recycled. A major drawback with the method is the large volumes of solvents required, but these can also potentially be recycled (see Section 4.2.4).

Table 5: Small Scale (5 g) Batches of SNQ Prepared Using Different Solvent/Non-Solvent Combinations than NMP/Acetone

Batch	Picrite Batch[a]	Solvent Vol (mL)/ Temp (°C)/Stirrer[b]	Non-solvent[c] Vol (mL)/ Temp (°C)/Additive	Result/Comment
81/87	832	NMP 25/80/B	Acet 100, EtOH 100/25	Raspberries
85/87	832	NMP 25/80/B	Acet 100, EtOH 100/32/Tween[d]	Stir 300 r/min, 2.8 g irregular spheres
87/87	832	NMP 25/80/B	Acet 150, EtOH 50/17	Stir 450 r/min, large spheres
97/87	811	DMSO 20/80/A	Acet 200/20	Stir 180 r/min, no precipitate
99/87	811	DMSO 25/80/B	Acet 100, H_2O 100/20	No product till seeded, then gave needles
100/87	811	DMSO 25/80/A	Acet 100, H_2O 100/20/Tween[d]	Stir 320 r/min, needles
102/87	811	EG 75, DMSO 10/95/A	Acet 150, EtOH 50/38	Stir 320 r/min, no product after 3 h or after cooling to 7°C
103/87	811	EG 100, DMSO 5/95/B	Acet 150, EtOH 50/38	No product after 4 days. Addition of water, seeding and evaporation gave low density spheres
118/87	Lot 6	DMF 25/80/A	Acet 200/20	Stir 320 r/min, small raspberries
119/87	Lot 6	DMF 25/85/B	Acet 50/50	Cooling produced a few large spheres up to 4 mm diameter
120/87	X/12/40	DMF 25/85/A	Acet 200/50	Stir 320 r/min, cooling gave needles
121/87	X/12/40	DMF 25/80/B	Acet 50/50	Cooling gave needles
122/87	832	DMF 25/80/A	Acet 100/60	Stir at 320 r/min, cooling gave small raspberries
123/87	Lot 6	EG 50/95[e]/B	Acet 150/60	Cooling gave needles
124/87	Lot 6	EG 50/95/B	Acet 100/60	Cooling gave needles
125/87	791	DMF 25/80/A	Acet 200/50	Stir 320 r/min, cooling gave raspberries
126/87	791	DMF 25/80/A	Acet 100/50	Stir 320 r/min, cooling gave raspberries
127/87	791	DMF 25/80/A	Acet 50/50	Stir 320 r/min, cooling gave raspberries
128/87	791	DMF 25/80/A	Acet 100/20/Tween[d]	Stir 320 r/min, raspberries formed
129/87	Lot 6	DMF 25/80/A	Acet 200/55	Stir 320 r/min, lumpy spheres
130/87	831	DMF 25/80/A	Acet 100/35	Allow to cool gave raspberries
131/87	X/12/40	DMF 25/80/B	Acet 200/50	Needles

Batch	Picrite Batch[a]	Solvent Vol (mL)/ Temp (°C)/Stirrer[b]	Non-solvent[c] Vol (mL)/ Temp (°C)/Additive	Result/Comment
132/87	X/12/40	DMF 25, DMSO 1/80/B	Acet 200/55	Stir 320 r/min gave needles
133/87	X/12/40	DMF 22, DMSO 3/80/B	Acet 200/55	Stir 320 r/min gave needles
134/87	X/12/40	DMF 20, DMSO 5/80/B	Acet 100/55	Stir 320 r/min gave needles
135/87	X/12/40	DMF 22, DMSO 3/80/B	Acet 50/55	Stir 320 r/min gave needles
192/87	Lot 6	EG 100/80[f]	Acet 100/52/Tween[d,f]	No product formed. Addition of 50 mL water gave needles
195/87	Lot 6	DMF 25/75	Acet 100/50/Tween[d,f]	Medium to large raspberries
196/87	Lot 6	DMSO 20, H_2O 50/75	Acet 200/49/Tween[d,f]	No product. Addition of water gave needles
197/87	Lot 6	Pyr 20[g], NMP 40/75	Acet 200/49	Rough spheres
136/87	Lot 6[h]	DMSO 25/80/A	Acet 200/50	Spheres after cooling in ice bath and seeding, 320 r/min stirring

[a] Refer to Table 2.

[b] A is stirrer depicted in Figure 1a, B that in Figure 1b.

[c] Acet = acetone, EtOH = ethanol, H_2O = water, DMF = dimethylformamide, EG = ethylene glycol.

[d] 3 drops of Tween dissolved in non-solvent.

[e] Under these conditions some decomposition of NQ was noted.

[f] Starting at this batch surfactant was added to the solvent, not non-solvent (although listed under non-solvent). In addition stirrer type was not noted.

[g] Picrite would not all dissolve, NMP added to complete solution.

[h] 10 g used.

Table 6: Large Scale Preparations of SNQ Using NMP/Acetone

Batch No.	Picrite mass (g)/Batch[a]	NMP Vol (mL)/ Temp (°C)/Stirrer[b]	Acetone Vol (mL)/ Temp (°C)/Additive[c]	Results/Comment
84/87	50/812	250/80/C	2000/15/Tween[d]	28.7 g of fine needle agglomerates
86/87	50/812	250/80/B	2000/34/Tween[d]	24.6 g. Aluminium foil placed over beaker to reduce acetone loss. Good spheres
88/87	50/812	250/80/A	2000/21	26 g of large 1.5-2 mm spheres
90/87	50/812	250/80/C	2000/20	31.5 g, spheres after 1 h, fine material contaminated later
93/87	50/831	250/80/C	2000/10	Stir 600 r/min. After 1.5 h get spheres (10 g), additional 21 g fines after 2.5 h
95/87	50/811	250/80/A	2000/10	Stir 600 r/min, spheres and fines
137/87	50/732	250/80/A	2000/30	Stir 320 r/min, large spheres
138/87	50/793	250/80/B	1000/37	Slow stirring, large amount of product adhered to walls and stirrer, some spheres
141/87	200/HC6839	1000/70/D[e]	6000/35	131 g spheres 50-300 µm, low bulk density
143/87	200/HC6839	1000/70/D[e]	7000/25	130 g similar to 141/87
145/87	200/HC6839	1000/25/D[e]	6000/35/Tween[f]	Small rough spheres
147/87	250/HC6839	1000/25/D[e]	6000/35/Tween[g]	Small rough spheres
163/87	200/731	1000/75/D	6000/25	67 g large spheres, 49 g fines
171/87	200/Lot 6	1000/75/D	6000/25	15.5 g large spheres, 104 g very fine spheres
172/87	200/731	1000/75/D	6000/25	Very similar to 171/87
193/87	50/Lot 6	200/75	2000/26/Tween[c,d]	Medium large spheres
194/87	50/Lot 6	200/75	2000/49/Tween[c,d]	Large spheres
1/88	100/731A	400/75	4000/35/Tween[c,h]	65 g spheres 500-600 µm
2/88	100/731A	400/75	4000/35/Tween[c,g]	Seeded with 1 g 1/88. 64 g spheres

[a] Refer to Table 2

[b] A, B and C refer to the stirrers depicted in Figures 1a, b and c respectively. D refers to the specialized pan shown in Figure 2

[c] After Batch No. 193/87 the surfactant was added to the NMP, not the acetone, although it is continued to be listed in the acetone column

[d] 30 drops added

[e] Solution filtered before addition to acetone

[f] 3 mL added

[g] 1 mL added

[h] 10 drops added

4.2.4 Preparation Using Recycled NQ or Solvents

An unresolved problem with the solvent/non-solvent process reported by ICT is the inability to recycle the mother liquors. Apparently "strawberries" or "sea urchins" are produced in preference to spheres. This represents a major problem since large quantities of recycled solvent would need to be purified, and residues disposed of, if the residual solution (saturated in NQ) could not be fed back into the process.

We accordingly chose to examine all aspects of the use of recycled reagents with the exception of solvent purification. The aim was to use minimal pretreatment. Four separate facets were investigated.

(i) Recycled NQ, i.e. an NQ product batch which had failed to form good quality SNQ under the conditions investigated.

(ii) Recycled NMP. These were the NMP residues remaining from the mother liquors after the acetone was allowed to evaporate at ambient temperature, and contained some dissolved NQ.

(iii) Recycled "acetone". These were mother liquors isolated from a previous SNQ preparation and were saturated in NQ.

(iv) Recycled NMP and "acetone" together.

The complete series of experiments are listed in Table 7. The results can be summarized below.

(i) Both original and recycled picrite gave very similar results; compare 150/87 and 152/87 to 149/87 and 151/87 in Table 7. This is hardly surprising since precipitation will not reduce the picrite purity.

(ii) Only three batches were attempted using recycled NMP with pure acetone, and the results were variable.

(iii) Use of recycled "acetone with pure NMP gave poorer quality spheres than would have been expected if pure acetone was used.

(iv) Use of both recycled NMP and "acetone" gave poor results.

It is concluded that NQ needles and unsuitable SNQ spheres could be recycled to give good SNQ. Use of mother liquors from one batch in a following batch is not likely to yield good quality SNQ without some purification of the solvent. Further investigation of this aspect could be undertaken in the future.

Table 7: Preparations Using Recycled Picrite, NMP or Acetone Recovered from Previous Batches[a]

Batch No.	Picrite Mass (g)/ Batch[b]	NMP Vol (mL)/ Temp (°C)/Stirrer[c]	Acetone Vol (mL)[d]/ Temp (°C)/Additive	Results/Comment
Recycled Picrite				
150/87	5R	25/75/A	200/28	Low density spheres, similar to 149/87 (see Table 1)
152/87	5R	25/75/A	200/28/Tween[d]	Low density spheres, similar to 149/87 (see Table 1)
153/87	5R	23[e]/75/A	200/27	Low density spheres, similar to 149/87 (see Table 1)
154/87	5R	24[f]/75/A	200/40/Tween[d]	Good spheres
155/87	5R	25/75/A	200/45	Good product
156/87	5R	25/75/A	200/45/Tween[d]	Small spheres
157/87	5R	24[f]/75/A	200/45	Small spheres, not a regular shape as 156/87
159/87	5R	24[f]/75/A	200/25/Tween[d]	Good small spheres
162/87	2R + 3/Lot 6	25/75/A	160/20	Large spheres
176/87	5R	25/65/A	200/23	Small spheres
177/87	5R	25/60/A	200/28	Raspberries
92/87	50R	250/80/A	2000/10	Stir 600 r/min, small spheres after seeding with fine material
Recycled NMP				
179/87	5/Lot 6	35R/75/A	200/23	Small spheres and fines
199/87	5/Lot 6	40R/75/A	200/49/Tween[d,g]	No product obtained
91/87	50R	420R/80/C	2000/5	Stir 320 r/min, good spheres
Recycled Acetone				
82/87	5/832	25/80/A	100R/40/EtOH 100R	Mother liquors (ML) from 81/87. Small rough spheres and agglomerates
83/87	5/832	25/80/A	200/23	No product after 45 min, cool to 15° and add ML from 82/87 gave small spheres and agglomerates
94/87	50/831	250/80/A	2000R + 500/23	ML from 91/87. No product even after seeding
140/87	50/793	420/80/A	1000R + 1000/20	ML from 138/87. Spheres and fines
142/87	200/HC6839	1000/70[h]/D	6000R + 400/30	ML from 141/87. Needle agglomerates

Batch No.	Picrite Mass (g)/ Batch[b]	NMP Vol (mL)/ Temp (°C)/Stirrer[c]	Acetone Vol (mL)[d]/ Temp (°C)/Additive	Results/Comment
144/87	200/HC6839	1000/20[h]/D	7000R/20	ML ex 143/87, needle agglomerates
146/87	200/HC6839	1000/25[h]/D	7000R/20/Tween[i]	ML ex 145/87 plus 3 g 144/87 seeding. Spheres but with rough and crystalline protrusions
148/87	200/HC6839	1000/25[h]/D	7000R/30	ML ex 147/87. Similar to 146/87 plus poor material
169/87	150/Lot 6 + 50/HC6839	1000/75/D	2000R + 4000/27	No product obtained
Both NMP and Acetone Recycled				
89/87	30/831	250R/80/A	2200R + 500	ML ex 88/87, stir 600 r/min, spheres after seeding
96/87	40/811	250R/80/A	2000R/10/EtOH 200	ML ex 93/87, stir 600 r/min, spheres and fines after seeding
139/87	50/732	420R/80/A	2200R/37	ML ex 137/87, rough low density spheres plus fines
170/87	120/731A	1500R/75/D	2000R + 4000/26	Lumpy agglomerates after seeding with 163/87 material

[a] R in the Table refers to recovered.
[b] Refer to Table 2.
[c] A, B and C refer to the stirrers depicted in Figures 1a, 1b and 1c respectively. D refers to the specialized pan and stirrer shown in Figure 2.
[d] 3 drops added.
[e] 2 mL of DMSO added.
[f] 1 mL of DMSO added.
[g] Added to NMP, not acetone.
[h] Solution filtered before addition to acetone.
[i] 6 mL added to acetone.

4.3 Aqueous Preparation Methods

As discussed in Section 3, an aqueous preparation method would be preferable. All the methods which we chose to investigate involved dissolving the picrite in an aqueous solvent combination in which it was reasonably soluble at 75 to 90°C, then cooling with stirring to crystallize out the product. This can be contrasted with the solvent/non-solvent method described in the previous sections. The complete list of experiments is detailed in Table 8.

Table 8: Attempts to Prepare SNQ on a 5 g Scale Using Aqueous Conditions

Batch No.	Picrite Batch[a]	Crystallization Reagents Water Vol (mL)/Other Solvent(s)[b], Vol (mL)/Stirrer[c]/Additive(s)	Temp (°C) Initial/Water bath[d]	Result/Comment
66/87	832	125/EtOH 100/A/gelatine[e]	75/55	Cooled slowly to 35°, raspberries and agglomerates
67/87	832	200/nil/B/dextrin[e]	90/30	Needles
68/87	832	200/EtOH 50/B/dextrin[e]	90/30	Needles
69/87	832	125/ETOH 50/A/phos[f]	90/55	Needles
70/87	832	125/EtOH 100/A/Tween[g]	75/55	Needles
71/87	832	125/EtOH 100/B/gelatine[h]	75/45	Needles
72/87	832	100/EtOH 100, EG 25/A/gelatine[e], dextrin[e], Tween[g]	78/45	Agglomerates
73/87	832	100/EtOH 200, DMSO 15/A/gelatine[e], phos[f]	78/45	Agglomerated spheres
74/87	832	100/EtOH 100, NMP 10/A/MC[i], gelatine[j]	78/45	Agglomerates with fan shaped particles
75/87	832	100/EtOH 100, DMSO 20/B/phos[f]	78/45	Agglomerates
104/87	811	100/EtOH 100/A/gelatine[c]	80/15	Stir 180 r/min. Rounded agglomerates
105/87	811	100/EtOH 100, DMSO 5/A/phos[f], gelatine[e]	80/15	Stir 180 r/min. Needles and needle agglomerates
106/87	811	100/EtOH 100/A/phos[f], Tween[g], gelatine[k]	80/47	Stir 320 r/min. Seeding necessary, needly agglomerates
107/67	811	100/EtOH 100, DMSO 15/A	80/55	Repeat of 73/67. Crystal agglomerates and some rounded material
108/87	811	100/EtOH 200, DMSO 15/A	80/50	Stir 320 r/min, fine needles
109/87	811	50/EG 75, Acet 100/A/dextrin[e]	80/0	Stir 320 r/min, needles
110/87	811	100/EG 50, MeOH 100/A/Tween[g], dextrin[e], gelatine[e]	75/15	Stir 320 r/min, low yield of spherical material
111/87	X/12/40	100/EG 50, MeOH 100/A/Tween[g], gelatine[e]	75/15	Stir 320 r/min, needly agglomerates
112/87	X/12/40	100/EG 50, MeOH 100/A/dextrin[e], Tween[e], gelatine[j]	75/15	Stir 320 r/min, crystalline agglomerates
113/87	Lot 6	100/EG 50, MeOH 100/B/gelatine[e], Tween[g]	75/15	Small round particles

Batch No.	Picrite Batch[a]	Crystallization Reagents Water Vol (mL)/Other Solvent(s)[b], Vol (mL)/Stirrer[c]/Additive(s)	Temp (°C) Initial/Water bath[d]	Result/Comment
114/87	Lot 6	100/EG 50, MeOH 100/A/gelatine[j], Tween[g]	75/15	Stir at 320 r/min, rounded but irregular product
115/87	Lot 6	100/EG 50, MeOH 100/B/gelatine[e]	75/15	Quite good rounded product
116/87	Lot 6	25/EG 50, MeOH 200, DMSO 3/B/gelatine[m]	50/50	Cooling produced low density spheres with amorphous material
117/87	Lot 6	100/EG 50, EtOH 200/B/gelatine[j], Tween[g]	50/50	Needle agglomerates

[a] Refer to Table 2.
[b] EtOH = ethanol, EG = ethylene glycol, DMSO = dimethylsulfoxide, Acet = acetone, MeOH = methanol.
[c] A is stirrer depicted in Figure 1a, B that in Figure 1b.
[d] Initial is the temperature the solutions are heated to to dissolve the NQ, then this solution is placed onto a water bath at the temperature shown and cooled with stirring to ambient temperature.
[e] 0.5 g dissolved in aqueous solvent.
[f] 3 drops of Phospholan PDB-3 added.
[g] 4 drops of Tween added.
[h] 2 g dissolved in aqueous solvent.
[i] Methyl cellulose, 2.5 g dissolved in aqueous solvent.
[j] 0.25 g dissolved in aqueous solvent.
[k] 1.0 g dissolved in aqueous solvent.
[l] 6 drops of Tween added.
[m] 0.1 g dissolved in aqueous solvent.

The solvent used in nearly all experiments was water with an alcohol (ethanol, methanol, EG) and an additive. The typical product morphology was needles or crystal agglomerates. In a number of cases rounded to spherical material was obtained, e.g. batches 73/87, 104/87, 113-116/87. Addition of DMSO or acetone did not markedly improve the product.

Although some promising results were obtained, it seems likely that much additional effort would be required to achieve consistent SNQ product. In the light of the lack of success also experienced by the German researchers, this is probably not a fruitful area for future studies.

Table 9: Preparations Using Acetone/NMP with Seeding to Produce Various Particle Size Spheres

Batch No.	Picrite Mass (g)/ Batch[a]	NMP Vol (mL)/ Temp (°C)	Acetone Vol (mL)/Temp (°C)	Seed SNQ Batch [mass (g)]	Result/Comment
165/87	200/Lot 6	1000/75	6000/25	141/87 [120]	247 g, small irregular spheres
166/87	200/731A	1000/75	600024	143/87 [120]	257 g, small spheres, bulk density 1.0
167/87	200/Lot 6	1000/75	2000 + 5000R[b]/25	145/87 + 147/87 [290]	391 g, small rough spheres, bulk density 0.9
168/87	240 R	1000/75	2000 + 4000R/25	163/87 [49]	Seed crystals fines. Crystalline agglomerates obtained
173/87	120/Lot 6	800/75	4000/25	171/87 [50]	Lumpy spheres
174/87	120/Lot 6	800/75	4000/25	171/87 [10]	Seed crystals fines, small spheres obtained
175/87	300/Lot 6 + HC6839 + 731A	2500R/75	5000/36	168/87 [47]	Spherical agglomerates
4/88	100/731A	400/75[c]	4000/35	1/88 [65]	Seeds all > 300 µm, 124 g spheres
5/88	100/731A	400/75[c]	4000/35	4/88 [40]	Seeds all > 600 µm, 96 g spheres
6/88	100/731A	400/75[c]	4000/35	5/88 [52]	Seeds had fines sieved out, 65 g spheres > 1 mm, 40 g fines < 300 µm
7/88	100/731A	400/75[c]	4000/35	6/88 [65]	Seeds spheres, 85 g spheres obtained
8/88	100/731A	400/75[c]	4000/35	7/88 [83]	Spheres 110 g, total yield > 140 g
9/88	100/731A	400/75[c]	4000R[d]/20	8/88 [110]	Spheres > 1 mm over 140 g, 27 g small spheres
10/88	100/731A	400/75[c]	4000/20	9/88 [140]	58 g of spheres > 1.7 mm diam., 141 g > 1 mm
11/88	100/731A	400/75[c]	4000/20	10/88 [141]	140 g of spheres > 1.7 mm diam., 75 g < 1 mm
12/88	100 R	400/75[c]	4000/35	Mixed[e] [72]	Not recorded
13/88	100 R	400/75[c]	4000/35	12/88	164 g spheres > 600 µm, 17 g 300-600 µm
15/88	100 R	400/75[c]	4000/35	Mixed	105 g spheres > 1 mm, 67 g > 600 mm
17/88	100 R	400/75[c]	4000/35	15/88 [110]	233 g spheres 600 µm - 1.00 mm

Batch No.	Picrite Mass (g)/ Batch[a]	NMP Vol (mL)/ Temp (°C)	Acetone Vol (mL)/Temp (°C)	Seed SNQ Batch [mass (g)]	Result/Comment
18/88	140 R	560/75[c]	5500/35	> 1.0 mm[f] [50]	69 g spheres > 1 mm, 78 g 150-300 µm
19/88	140 R	560/75[c]	5500/35	18/88 [66]	85 g spheres > 1 mm, 54 g 150-300 µm
20/88	100 R	400/75[c]	4000/35	> 1.0 mm[f] [50]	86 g spheres > 1 mm, 45 g 150-300 µm
22/88	100 R	400/75[c]	4000/35	20/88 [50]	114 g spheres > 1.7 mm
23/88	100 R	400/75	4000/35	> 1.0 mm[f]	107 g spheres > 1.7 mm
27/88	240/Lot 6	1000/75	4000/35	> 1.0 mm[f] [85]	218 g spheres
28/88	240/Lot 6	1000/75	4000/25	> 355 µm[f] [109]	255 g spheres
30/88	240/731A	1000/80	4000/20	> 600 µm[f] [127]	
31/88	240/731A	1000/80	4000/20	> 600 µm[f] [115]	74 g spheres > 1.7 mm, 72 g > 600 µm but < 1.7 mm, 125 g fines
32/88	140/Lot 6 + 100 R	1000/80	4000/35	31/88[g] [65]	168 g spheres, no fines
33/88	100/Lot 6 + 140 R	1000/80	4000/35	> 1.00 mm[f] [148]	230 g spheres > 1.7 mm

a Refer to Table 2. R = recovered from a previous unsuccessful batch.
b Mother liquors ex 166/87.
c 10 drops of Tween.
d Mother liquors ex 8/88.
e 300-600 µm sieve fraction from various SNQ batches.
f Sieve fractions from various SNQ batches.
g > 600 µm, < 1.7 mm.

4.4 Growth of SNQ to Produce Larger Particle Sizes

A standard method of inducing crystallization is to add small quantities of the crystalline product material as nucleation sites, thereby "seeding" crystallization. Alternatively larger amounts of product can be added to the saturated solution, causing these crystals to grow by deposition from solution onto their surface.

Although seeding was used in a few cases, e.g. batch 160/87, Table 3, the major thrust was to increase the size of successive SNQ products by growth from deposition. The complete series of experiments is listed in Table 9.

A first observation to make is that if the seeding crystals are not spheres, good quality spheres are not usually obtained (refer to batches 167/87, 168/87, 173/87 and 174/87). It also can be seen that good quality large spheres must start by growing from good quality smaller spheres.

Most of the batches from 4/88 onwards were used to grow larger spheres by using the previous batch as seed material. In this way quite large spheres, diameter over 1 mm, could routinely be grown in high yield. Spheres of this size were required for formulation studies with TNT.

4.5 SNQ Material Properties

4.5.1 Particle Size Distribution of Individual Batches

Particle size distributions obtained by sieve sizing for a series of SNQ batches produced under a range of experimental conditions are detailed in Table 10. The majority of the batches have a narrow particle size distribution limited to one or two sieve sizes. The exceptions are 198/87 and 200/87, which are of smaller average particle size and the choice of sieves meant that more (than two) were required to cover the range, while 18/88 and 19/88 had a bimodal distribution.

Table 10: Particle Size Distribution of SNQ Batches

Batch No.	% Retained on Sieve of Aperture Size as Shown									
	2.36 mm	1.70 mm	1.00 mm	600 µm	300 µm	150 µm	106 µm	75 µm	45 µm	< 45 µm
193/87	-	-	-	20.8	78.8	0.4	-	-	-	-
194/87	-	-	100	-	-	-	-	-	-	-
198/87	-	-	-	-	6.1	69.7	3.0	3.0	15.2	3.0
200/87	-	-	-	-	-	-	60.7	12.4	22.6	4.3
13/88	-	-	-	90.6	9.4	-	-	-	-	-
15/88	-	-	61.3	38.7	-	-	-	-	-	-
17/88	-	-	-	100	-	-	-	-	-	-
18/88	-	-	46.9	-	-	53.1	-	-	-	-
19/88	-	-	61.2	-	-	38.8	-	-	-	-
22/88	-	100	-	-	-	-	-	-	-	-
23/88	-	100	-	-	-	-	-	-	-	-

All the conditions/methods from batch 13/88 onwards were designed to grow increasingly larger particles by using selected portions of the previous batch as seed material. This has resulted in the general trend to larger particles as batch numbers increase. The bimodal batches 18/88 and 19/88 result from larger spheres formed via growth on the seed material while the smaller size fraction presumably forms in a competing process from new nucleation.

Batches 193/87 to 200/87 in Table 10 result largely from the different acetone temperatures (refer also to Table 4); the higher the temperature, the larger the particle size (see discussion p.14 also).

4.5.2 Bulk Density of SNQ Batches and Sieve Fractions

The bulk density of many SNQ batches was routinely determined in a qualitative way by tipping the entire batch into a measuring cylinder and tapping to achieve a minimum volume. Values of 0.95 to 1.0 g/mL were normal, although occasional batches with much lower bulk densities, around 0.75 g/mL, were obtained. These low density batches consisted largely of a mixture of small spheres and non-spherical particles. For comparison, the maximum bulk density for HDNQ produced by gelatin modified recrystallization was 0.87 g/mL [11].

Accurate bulk densities were determined using the method described in Section 3.4. These are listed in Table 11 for selected SNQ batches, four "unimodal" sieve fractions and a bimodal sieve fraction blend. The results for the batches reinforce the description in the previous paragraph. The unimodal sieve fractions had slightly higher bulk densities (1.03 to 1.07 g/mL) which were independent, within experimental error, of particle size. The lack of dependence on particle size is expected on the basis of a previous report [29].

Table 11: *Bulk Densities for Selected SNQ Batches, Unimodal Sieve Fractions and a Bimodal Blend*

SNQ Sample	Bulk Density (g/mL)
Batch 85/87	0.76
Batch 86/87	1.00
Batch 91/87	1.00
Batch 165/87	1.00
Batch 166/87	0.90
Batch 167/87	0.74
Batch 171/87	0.94
Batch 172/87	1.01
Batch 173/87	1.01
Batch 174/87	1.01
Sieve Fraction 180-300 µm	1.06
Sieve Fraction 300-600 µm	1.07
Sieve Fraction 600 µm - 1.00 mm	1.05
Sieve Fraction 1.7 - 2.36 mm	1.06, 1.03
Bimodal Sieve Fraction Blend	
1.7 - 2.36 mm/150-300 µm 68:32	1.40, 1.39

HDNQ, even at the maximum bulk density of 0.87 g/mL, could only be incorporated into molten TNT at 40% w/w; the slurry became unpourable at higher NQ levels [5]. It is to be expected that the higher bulk density of SNQ would lead to higher levels of incorporation into molten TNT. Blending batches of different particle size will increase bulk density provided an appropriate small/large ratio is selected. A number of bimodal mixes were investigated; the maximum bulk density achieved was 1.40 g/mL for the blend of 1.70 to 2.36 mm spheres (68%) and 150 to 300 µm spheres (32%).

The theoretical packing volume fraction for a close packed arrangement of uniform spheres is 0.7405 [30]. The bulk densities for the unimodal samples in Table 11 correspond to a packing volume fraction of slightly less than 0.6, indicating that the close packed arrangements were not achieved. Instead they approximated a double staggered arrangement where the theoretical packing volume fraction is 0.6045 [30]. This results from some of the SNQ particles not being spherical, therefore disrupting the array.

Bimodal distributions have a theoretical packing volume fraction of 0.845, representing the hexagonal close packed array with interstices filled for at least a sevenfold difference between sphere diameters. The maximum bulk density blend, 1.40 g/mL, has approximately ninefold size difference between the spheres but the packing volume fraction is only 0.787. The discrepancy again can be explained by the fact that all the SNQ particles were not perfectly spherical.

4.5.3 SNQ Morphology

A number of the ICT publications, e.g. ref. [15], include good photomicrographs and scanning electron micrographs of SNQ. Accordingly, comments will be limited to those providing some insight into the mechanism of their formation.

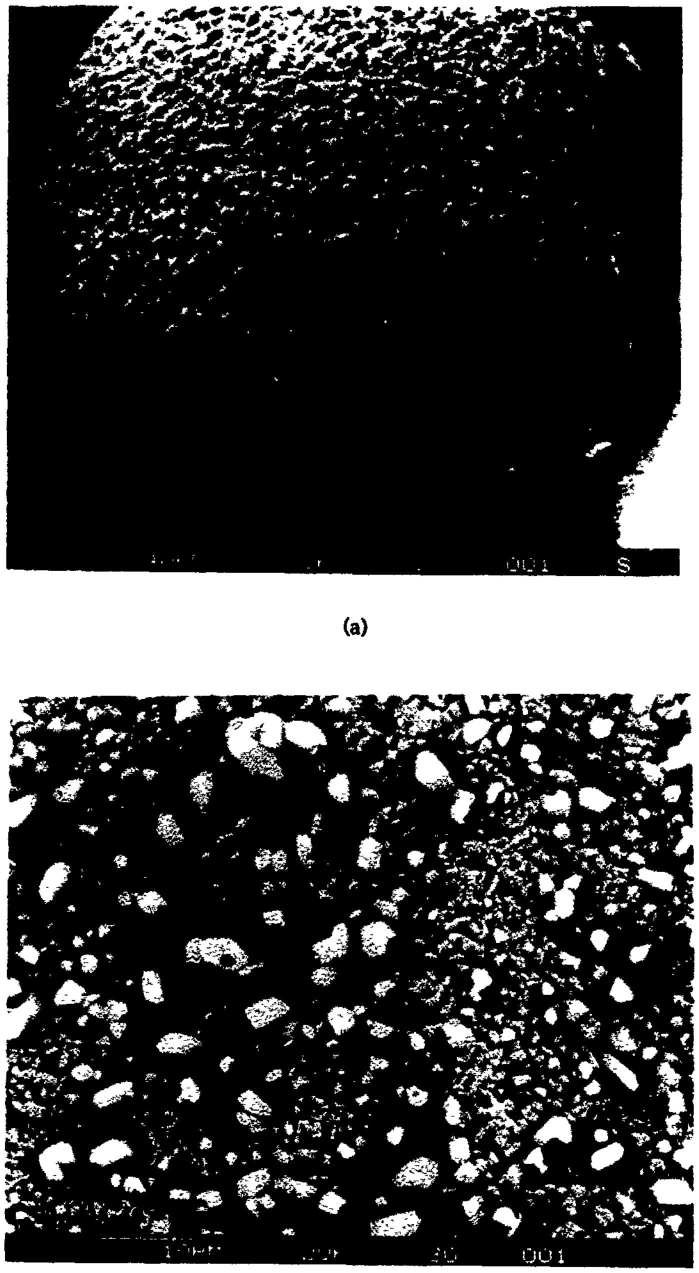
Photomicrographs of good spheres, such as shown in Figure 3a, suggest smooth surfaces, but higher magnification obtained by SEM shows the surface to be rough (Fig. 4). Cleavage of spheres indicates a central growth point (Fig. 5). All this evidence is consistent with the mechanism of formation being by radiation of needle-like particles from a central and single crystallization nucleus. Radiation must be approximately constant in all directions to give the relatively smooth surfaces obtained on the spheres, with dendritic growth of the needles to fill any voids as they radiate outwards.

Some particles clearly originated from more than one nucleating site (Fig. 6). It may be that in these cases two spheres have coalesced during growth and continued to grow as a unit from their individual growth centres.

Growth of larger SNQ particles by seeding results in concentric growth as shown in Figure 7. This particular sphere has been grown a number of times to achieve the size shown (approximately 2 mm diameter). Each ring represents a separate growth operation.

4.5.4 Hazards Assessment: Thermal Stability and Impact Sensitiveness

Results are listed in Table 12 for vacuum thermal stability and ignition temperature, and in Table 13 for Rotter F of I, for selected batches of SNQ and picrite.



(a)

(b)

Figure 4: Scanning electron micrographs of the surface of a single SNQ particle, indicating that growth is approximately constant in all directions.

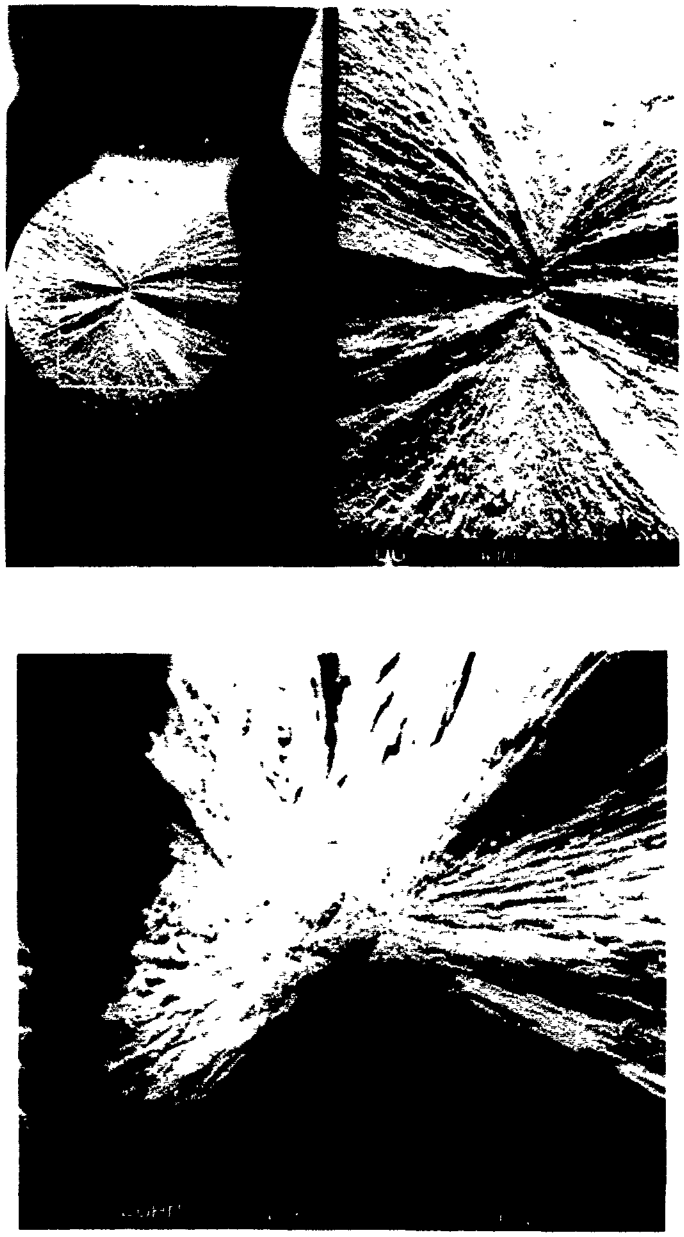
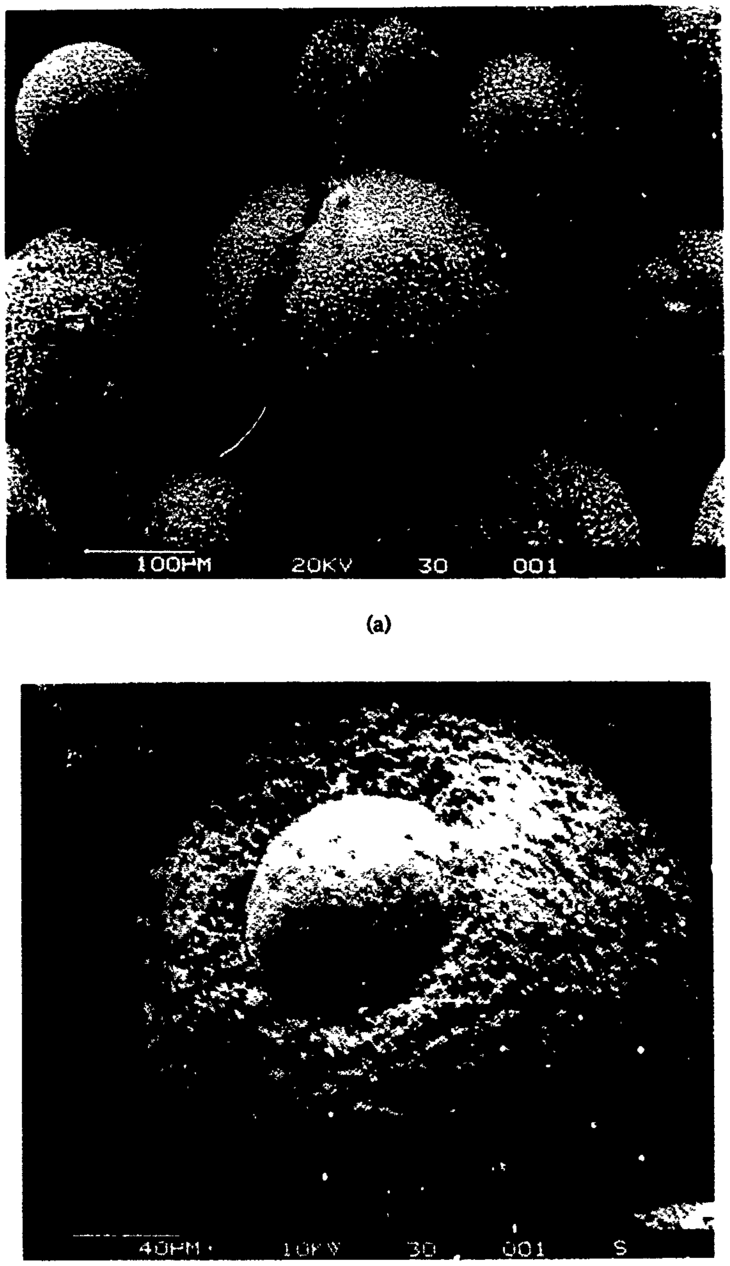


Figure 5: Scanning electron micrographs of cleaved SNQ spheres, showing internal structure with needle-like particles radiating out from a central growth nucleus.



(a)

(b)

Figure 6: Scanning electron micrographs of SNQ particles showing evidence of more than one nucleating point.

Figure 7: Sectioned SNQ particle produced by the large scale method using seeding. The concentric growth rings can be clearly seen.

Table 12: Vacuum Thermal Stability and Ignition Temperature Results for SNQ and Picrite Batches

Sample	Vacuum Thermal Stability mL gas evolved for 5 g at 120°C for 40 h	Ignition Temperature 0.25 g heated at 5°C/min
SNQ Batch 86/87	0.5	
SNQ Batch 165/87	0.3	230 (faint smoke, continues to 380°C)
Picrite Batch 731A	0.3	221 (smokes)
Picrite Batch X/12/40	0.4	

Table 13: Rotter Impact Sensitiveness Test Results for SNQ and Picrite Batches

Sample	F of I (average gas evolved, mL)	Comment
SNQ Batch 165/87	120 (0.8)	
SNQ Batch 140/87	180 (0.9)	Spheres crushed before testing
Picrite Batch X/12/40	100 (1.8)	
Picrite Batch 731A	105 (2)	
Picrite Lot 6	120 (1.5)	F of I changes to > 180 after desiccation for 5 days
Recrystallized Picrite	> 200	Recrystallized from water and dried (at MRL)

The results in Table 12 indicate that SNQ has excellent thermal stability, very similar to picrite. Any residual occluded solvent has not reduced stability. Ignition temperatures are as expected, although neither picrite nor SNQ proceed from smoke to flame under the test conditions.

F of I values are lower than expected but accompanied by very low gas evolution; if the ignition criterion had been > 1 mL gas evolution, they would have been rated less sensitive (higher F of I). The results for picrite can be very dependent upon conditioning of the sample; the F of I for Lot 6 picrite changes from 120 to > 180 after desiccation for 5 days, while recrystallization from water followed by drying raises the F of I above 200. More detailed assessment of SNQ and other insensitive high explosives has recently been carried out using the Rotter explosiveness test and relative hazard has been determined to be very low [31].

5. Conclusions and Future Directions

Propellant grade picrite used in Australian production can be readily converted into a spherical form (SNQ) which exhibits high bulk density and good packing. It would be expected that incorporation of at least 60% w/w SNQ into TNT could be achieved to give a readily melt-castable filling with vulnerability much lower than Composition B. Upgrading of the SNQ production process from batch to continuous has been described in a recent patent from ICT [16]. This would represent a very significant advance in both ease and economics of production.

The use of NQ in high explosive formulations has usually not proceeded to Service introduction in the past. This probably results from relatively low performance; although NQ has a high VOD, the pressure/time function is reduced by the high water content of the detonation products. In addition there has been doubt about the ability of the TNT and NQ detonations to effectively "couple"; output is consistently less than theoretically predicted.

However, SNQ should confer reduced vulnerability, and for this reason its use is being investigated in melt-cast formulations in a number of countries as an alternative to cast-cured PBXs, particularly for large munitions such as bombs. One company pursuing this goal is Explosive Research and Development Corporation (ERDCO) in the US. ERDCO, who initiated contact with us, are developing insensitive GP bomb fills using SNQ as one of the ingredients; a patent has recently been granted [32]. USAF are developing TNT/SNQ-based fillings for GP bombs, and RAAF is also examining its policy on its future bomb inventory.

Research to determine the rheology of SNQ suspensions in molten TNT to maximize the level of SNQ while ensuring processibility has recently been completed at MRL. Performance measurements on cast charges will also be undertaken. Long term storage of SNQ also warrants attention; it has been reported to grow "whiskers" on storage. NQ is known to decompose very slowly to evolve ammonia, which may also be unacceptable in a TNT-based formulation.

Until these points have been investigated recommendations on suitability for applications such as bomb fills cannot be made.

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Conversion of Propellant Grade Picrite to Spherical Nitroguanidine,
an Insensitive Filler for Melt-Cast TNT Formulations

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ABSTRACT

The preparation of spherical nitroguanidine (SNQ) from Australian propellant grade picrite (NQ) has been investigated. A method based upon N-methylpyrrolidone (NMP) and acetone as solvent/non-solvent has been found to give a good quality SNQ product from a variety of picrite batches. Larger spheres can be grown under these conditions by controlled seeding. Attempts to use recycled NMP and acetone gave an unsatisfactory product in general. Use of aqueous based systems gave poor product. Particle size, bulk density and hazard properties are determined for a number of batches. Recommendations on future research to evaluate SNQ formulations as insensitive main charge explosives are outlined.

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