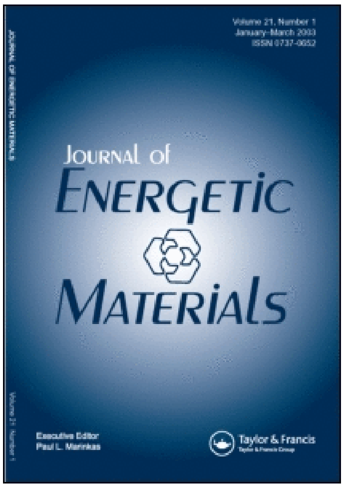

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EFFECT OF ADDITIVES ON THE NUCLEATION OF TNT

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ABSTRACT

The effect of a range of additives, derived from the substituted trinitrobenzene molecules, on the crystallisation of TNT has been investigated by Differential Thermal Analysis, x-ray diffraction, optical and electron microscopies. The distribution of the additive in the spherulites was investigated by electron induced x-ray fluorescence. The modification of grain size and distribution accompanying a reduction in supercooling have been studied and a comparison with the effect of ultrasonics on munition filling made.

INTRODUCTION

Trinitrotoluene or 1-methyl,2,4,6,-trinitrobenzene, TNT has wide spread use as a high explosive filling due to its low cost, low sensitivity to accidental initiation during manufacture and , because of it low melting temperature, 80°C, the availability of safe, steam heated, melt casting procedures . Some properties of TNT cause problems with the completed munition. There is a difference of 11 % between the densities of the

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solid and liquid forms [1] whilst in the solid state TNT an exist two crystal morphologies, monoclinic and orthorhombic [2,3]. Both the monoclinic and orthorhombic structures form a number of polytypes identified by different unit cell stacking along the 'a' axis giving rise to additional superstructure reflections in their x-ray diffraction patterns [4,5]. These can be indexed using unit cells with two and four times the normal unit cell 'a' dimension. As a result some powder pattern reflections show variable intensities, which depend on the conditions under which the sample were grown. Pure liquid TNT exhibits extensive supercooling during the setting process. This latter property causes TNT to crystallize in highly orientated needle shaped crystals [6]. Coefficients of linear thermal expansion along the needle's short and long crystallographic axial directions differ by a factor of almost four ("a" and "c" directions ~ 5 x 10^{-5} mm mm^{-1} $^{o}C^{-1}$ "b" direction 18.1 10^{-5} mm mm^{-1} $^{o}C^{-1}$) [7]. These thermal properties of the needle shaped crystals causes problems in munition fillings by creating voids , either during cooling or on thermal cycling, which can cause premature initiation during firing of shells or missiles. These problems have been extensively studied and solutions involving heat cycling of the filling, sometimes in the presence of additives, have been proposed [8]. The most successful of the treatments, involving the use of hexanitrostilbene, HNS, additive is the subject of a patent granted to the Bofors company [9]. The treatment produces the random distribution of small size, evenly shaped, solid particles required for the optimum munition filling. The mechanism by which the HNS operates has been the subject of a number of studies [10,11,12,13]. A complex formed between TNT and HNS with 2:1 stoichiometry has been postulated based mainly on thermal analysis of the " purified " nucleant and limited x-ray diffraction data using a limited number of lines from the powder pattern (insufficient to characterise the unit cell) [11]. Differences between the nucleant powder pattern and a simple sum of those from the components is insufficient to draw any positive conclusions. There is conflicting evidence regarding the formation and thermal stability of the complex [9,14]. This paper reports our studies of the effects of additives and thermal treatment on the particle size distribution and crystal structure of the solid produced during the setting of molten TNT. All the additives used were based on the trinitrobenzene molecule, with various substituents in the 1 position of the benzene ring. Similarity in structure between the additive and TNT could enable the additive to occupy the face of the growing crystal and hence inhibit the rapid growth of the crystal along the needle axis [15]. The best predictions are made when the modifications on the substrate are minor. Introduction of small steric hindrances or minor alterations in molecular planarity can have the desired effect. Incorporation of 1% benzamide suppresses the growth of benzoic acid along the 'b' axis and the crystals develop along the 'a' axis [16] . It was anticipated that the rapid supercooling could be eliminated whilst maintaining the explosive performance. Investigation was by setting point determination, x-ray diffraction, differential thermal analysis (DTA), optical and electron microscopies.

EXPERIMENTAL

a) Materials

Samples of TNT and HNS were supplied by the Special Products Division, Royal Ordnance Factory , Bridgewater. Picryl chloride, bromide and hydroxide (picric acid) were supplied by BDH Chemicals Ltd. Poole . Sodium picrate was prepared by a neutralisation reaction between "Analar" sodium hydroxide and stoichiometric quantities of picric acid using a Jencons pH meter and electrode type to indicate the equivalence point. Trinitrobenzoic acid was prepared by the chromic acid oxidation of TNT using established literature methods [17]

Purity of all materials, except sodium picrate, was checked by melting point and High Performance Liquid Chromatography . HPLC was performed on methanolic solutions of the compound using an ODS2 column on a CM400 system, supplied by Milton Roy Ltd., Mobile phases were mixtures of methanol and water 60/40 for TNT and 70/30 for the HNS. As a result of preliminary tests the TNT was purified by the method of Gey , Dalby and Van Dolah [18] , followed by recrystallization from methanol. HNS was recrystallized from N-methylpyrrolidone and washed with methanol. Both materials were vacuum dried for 24 hours, to remove any remaining solvent, prior to use. After purification, HPLC indicated all materials were better than 99.9 % pure.

Equipment and Sample Preparation

Samples containing additives were prepared by dry mixing the two components and then either performing a simple melt / solidification cycle at 85 ^{o}C and 120 ^{o}C or the Bofors cycle. Setting points were determined by measuring the temperature of a 5 g sample contained in a test-tube, surrounded by an air jacket, as it cooled from 85^{o}C, with a thermistor temperature sensor. The molten liquid was vigorously stirred until the increased viscosity, due to solid separating out, caused the stirring to induce voids in the mixture.

X-ray diffraction was performed on a Siemens D500 powder diffractometer using a copper target operated at 40 Kv and 30 ma. The diffracted beam was focussed onto the Geiger detector by a graphite single crystal monochromator. Diffractometer control and data capture were performed by an IBM AT computer operating under the ISIP software package [19]. Powdered samples of the materials studied were placed on a flat glass plate and mounted on the diffractometer in the Bragg Brentano focussing position [20]. During the data collection, samples were rotated through 180 degrees around the normal to the plane of the glass plate to reduce the effects of preferred orientation within the sample. Data was examined by the powder indexing program [21] and the optimum fit to the unit cell type determined

Thermal studies were performed on ~25 mg samples of the materials, contained in a platinum crucible, using a Stanton Redcroft STA 700 analyser . An equal mass of aluminium oxide Al_2O_3 was used as the inert reference material. Samples were analysed by thermal cycling between ambient and 150 ^{o}C at heating rates of 5 ^{o}C min^{-1} .

Optical microscopy was performed on a Mettler FP2 hot stage system mounted on a Reichert-Jung, "Polyvar" microscope. 50 mg samples of the materials contained on a standard microscope slide , were heated to 85 °C, given a brief stir with a small glass rod to ensure homogeneity and covered with a heated cover slip, which prevented premature cooling and solidification of the TNT. Glass fibres 40 μm thick placed between the slide and the cover slip ensured a constant specimen thickness . The specimen was then allowed to cool to ambient in a draught free enclosure. Other samples were heated to 120 °C and treated similarly, while a third series was quenched from 85 °C, on a liquid nitrogen cooled steel plate. The samples obtained were studied under the microscope and photographed to record the effect of additives and thermal history on the crystallinity of the TNT. The images of the slide contents were analysed by a Kontron IBAS 2000 Image analyser system, which contained a grain sizing program. This identified grain boundaries and calculated distribution of the average grain size. Output was a histogram of number of particles in given range against particle size.

A Joel JSM 840A Scanning Electron Microscope, fitted with a Link Systems 860 series 2 X-ray micro-analyser, was used to investigate the distribution of some additives within the solid grains by measuring electron induced x-ray fluorescence on samples after removal of the cover slip

RESULTS

Pure TNT set at 80.8 °C and exhibited about 2 °C supercooling, in spite of the stirring. All the additives tried reduced the setting point, as expected for impurities, and the supercooling. HNS was the most effective (supercooling 0.1 °C compared to > 0.5°C for the best of the others). During setting in the DTA, TNT exhibited, as expected , 20 °C supercooling . Additives reduced the supercooling, with the HNS being most effective as shown in figure 1, which compares the setting traces for pure (a) and HNS treated (b) samples. The temperature T and temperature difference δT traces are given. The sudden increase in the temperature trace, with the onset of setting, is characteristic of supercooling, as is the very abrupt leading edge to the accompanying exotherm.

Quenched samples exhibited some evidence of a phase transition during the first heating cycle. This was confirmed by the modified thermogram obtained from a mixture of annealed and quenched TNT figure 2a and also when a quenched sample was run against an annealed TNT sample as the standard figure 2b . A second heating cycle on the same sample gave an almost flat baseline as expected for two identical samples.

X-Ray Diffraction

Pure and methanol recrystallized TNT produced powder patterns which were consistent with the monoclinic unit cell. Typical powder diffraction traces for the monoclinic and orthorhombic forms are given in figure 3 . Dashed areas on the figures indicate the regions of differences between the two patterns. There are also small changes in peak positions and relative intensities between the monoclinic and orthorhombic forms. Figures of Merit [22] for unit cell fits to observed data indicate that only in the case of the sample quenched from 85 °C, was an orthorhombic cell the best fit.

Almost all of the additives produced powder diffraction patterns consistent with mixtures of the monoclinic and orthorhombic TNT cells contrary to other authors [23]. Even quenching of doped samples, from either 85 or 120 °C, did not produce pure orthorhombic material in contrast to the pure TNT samples. The exception was with HNS doped samples. These always produced monoclinic crystal structures.

Optical and Electron Microscopies

Pure TNT air cooled from 86 ^{o}C produced the crystals shown in figure 4 . The needle shaped crystals were part of a limited number of spherulites. The grain sizing program could not cope with the needle nature of the crystals due to the large dimension differences parallel and normal to the needle axes and the small number of data points. Grain size distribution limits produced were between 11.25 and 15.35 mm.. Photographs of the crystals obtained from TNT samples containing the soluble compounds picryl bromide, chloride and trinitrobenzoic acid, air cooled from 85 ^{o}C, are given in figures 5 (a)-(c). These show the presence of highly orientated spherulites growing from a limited number of nucleating sites. Histograms for the grain size distribution given by these TNT samples, figures 5 (d)-(f), show that the average grain size is distributed around 1200 μm with the picryl bromide producing the smallest average grain size. XRF indicated the additive was present, in the highest concentration, at the centre of the spherulite .

Sodium picrate was unusual in that , although it had low TNT solubility, it did not always act as the nucleating site, with the spherulite sometimes growing around the additive particles see figure 6. The (a) figure identifies the circled particle occluded by the spherulite and the (b) figure shows the sodium x.r.f. wavelength microprobe trace in the region of the spot. Quenching of these doped samples reduces average grain size to 900 μm and produced a more random crystal growth.

Samples containing 1% HNS showed the smallest grain size, largest number of nucleating sites and largest number of spherulites see figures 7 (a)-(f). Samples cooled from 85 ^{o}C had a mean grain size of 90 μm, whilst those cooled from 120 ^{o}C, had a mean grain size of 230 μm. Rapid quenching from 85 ^{o}C produced samples with a mean grain size of 32 μm, the smallest of all.

DISCUSSION

All additives reduced the supercooling with HNS being the most effective. At 1% HNS no super-cooling was visible on the DTA trace which, because of the lack of stirring, was the most sensitive measure for supercooling. The effect must be due to the wide distribution in nucleating sites in the presence of the HNS. Optical microscopy coupled with the grain sizing program indicated that all additives reduced the grain size of the cast samples and increased the number of spherulites produced on setting. Samples cooled from 120 ^{o}C produced larger grain size than samples cooled from 85 °C. This indicates that annealing and growth of the nucleating species occurs at the higher temperature reducing the number of nucleating sites available when the melt finally sets. Rapid quenching reduces the grain size of all materials and also generally produces a mixture of monoclinic and orthorhombic structured phases. When observed x-ray data are analysed as only one phase then poor figures of merit are obtained . If allowance is made for the presence of the second phase the figures of merit improve considerably. As an example the figure of merit for sample doped with TNBA improved to 2.6 to 12.1, when allowance was made for the presence of the second phase. HNS was unique in producing only the monoclinic phase under all conditions. Further examination of the x-ray powder patterns from these materials is required, before a complete understanding of the structures produced, can be obtained. There is considerable variation in line relative intensities between experiments but their positions do not change.

The cycle cast method produced the finest grain material apart from the quenched sample. Application of ultrasound to the setting sample was also trialled. Again although this method produced a fine grain high density material, see figure 8 , the complexity of the munition filling process using ultrasound prohibits its use . Individual shells would have to be attached to some ultrasound coupling device for the duration of the setting process and variation in quality of material produced due to incomplete coupling may be large. Quenching is not a viable technique for munition filling processes, because of the experimental difficulty associated with rapid cooling of bulk quantities, of low thermal conductivity materials, and also it produces low density fillings, which have a tendancy to void formation.

HNS addition above the 0.5% produced smaller grain size material but the improvement in the munition filling was marginal. The effect of thermal cycling, on the grain size of the cast TNT samples, may be due to changes in the size and nature of the HNS nucleating species induced by the thermal processes. Some additional experiments were performed using different particle size HNS crystals added to TNT followed by simple casting from 85 °C. Samples containing HNS crystals in the range 0.5 to 0.05 mm were coarse grained, whereas 60 μm HNS particles produced a finer grain material. However neither of these experiments matched the fine grain material produced by the HNS treated material subjected to the Bofors cycle cast method. Compare figures 9 and 7. This indicates that the nucleant is not pure HNS but some admixture between

HNS and TNT. Some authors have proposed a complex formed from 2 TNT and 1 HNS molecules as the nucleating species, but in view of the low mutual solubility of TNT and HNS complex formation would appear unlikely . Also the variable composition of the nucleant is unlike normal complexes [24]. The slow decomposition exhibited by the complex in the DSC is unusual. Normally charge transfer complexes exhibit rapid, almost instantaneous, thermal decomposition during thermal cycling [22]. Complexes formed between TNT and other nitrocompounds i.e. 2,4 dinitrotoluene and 1 nitronaphthalene generally exhibit dissociation temperatures below the melting points of either component. It would be unusual for the proposed complex to decompose above the melting point of one of the components TNT, without the other component demonstrating solubility in the TNT. The two, complex forming compounds, mentioned above are miscible with TNT in almost all proportions. Additives which were soluble in TNT produced clusters of nucleating sites. Hexanitobibenzyl, which has a similar molecular structure to TNT and is essentially two TNT molecules linked through the CH_3 groups with the elimination of H_2, has, in the solid state, an identical space group, $P\ 2_1/c$, to TNT and HNS but has different unit cell dimensions to both TNT and HNS [25]. See table overleaf

Compound	HNBB	TNT	HNS
Space Group	P $2_1/c$	P $2_1/c$	P $2_1/c$
'a'	5.991	21.23	14.693
'b'	8.134	6.08	5.585
'c'	18.087	14.958	22.159
ß	99.0	110.12	108.44

Although HNBB is quite soluble in liquid TNT it can act as a limited effect nucleant by restricting the supercooling and reducing the growth rate of the 110 face, which is responsible for the needle formation. Further work on this area is required. The critical parameters appear to be the comparitively strong interactions between the HNS molecules in solid HNS, which is responsible for the high melting point and lattice energy compared to TNT. The interaction between HNS and TNT must be weaker, hence the low mutual solubility. Although TNT and HNS appear to have similar solid structures, a more detailed examination shows extensive differences in the molecular stacking arrangements in the two solid [26,27] and hence incorporation of HNS into the TNT lattice would be energetically almost impossible, with the reverse operation being only marginally easier.

The importance of solid structure, as well as additive insolubility, on the effect of additives was demonstrated in experiments performed using sodium picrate or aluminium oxide powder. X-ray fluorescence indicated that the spherulites had grown around the particles of the solid and the solid had not acted as a nucleating site. The Al_2O_3 treated sample had a grain size identical to that of the pure TNT samples. It was noted, during the melting stage of the preparation, that a pink colour developed in the samples containing Al_2O_3. This may be due to the formation of a complex, analogous to red Meissenheimer complexes obtained from nitrocompounds and bases, but further investigation would be required to confirm this.

The solid state transition, between the monoclinic and orthorhombic phases of TNT, requires further investigation. The complex DTA trace observed, during the first heating cycle, when the annealed TNT sample is used as the standard and the quenched TNT as the sample, indicated that a transition between the phases occurs in the region of the melting point and that the melting points of the two phases may be different. Subsequent heating cycles produced an almost straight line trace, with minor deviation due to the imperfect matching of the two sample weights and the measurement mountings. Unfortunately the small differences in the x-ray powder pattern from the two phases renders the normal x-ray technique for phase transition studies unusable. Further research into the exact nature of the nucleant and its structure is required.

CONCLUSIONS

The crystallinity of TNT can be satisfactorily modified by the incorporation of limited solubility additives in the melt prior to casting. Grain size of the solid TNT is dependent on the thermal history during the latest thermal cycle. Higher temperatures produces larger grains. The structure size and composition of the nucleating species are important parameters in controlling the quality of the munition filling. Vigorous mechanical stirring or the application of ultrasound to the setting mixture provide alternatives to the use of the optimum additive HNS, but they require sophisticated procedures by skilled operators in contrast to the simple HNS casting procedure.

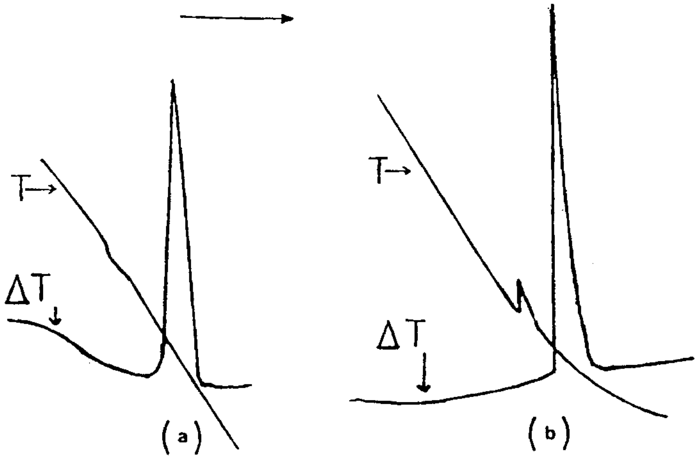

FIGURE 1
Comparison of DTA setting Traces for (a) HNS doped and (b) pure TNT. T and T traces are offset in space to prevent the recorder pens colliding

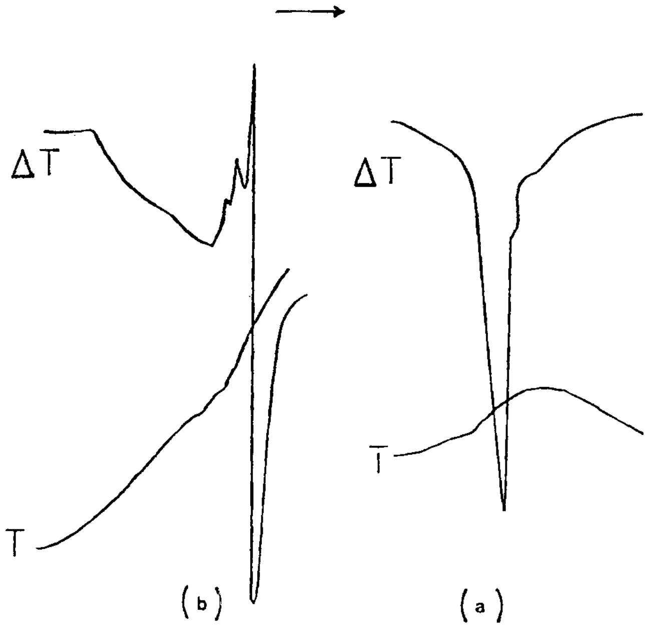

FIGURE 2
DTA endotherm trace for the melting of (a) a mixture of annealed and quenched TNT and (b) quenched TNT with annealed TNT as standard. There is a pen offset between T and T curves

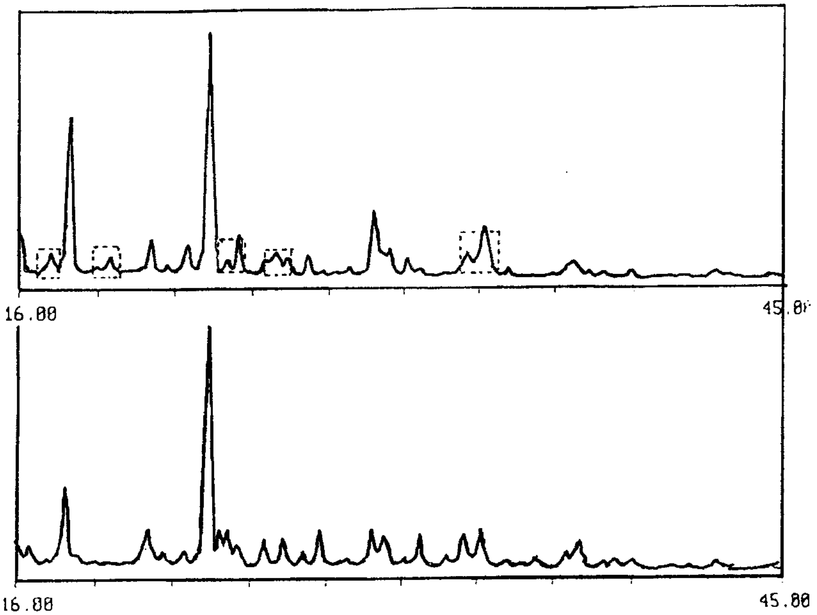

FIGURE 3
X-ray Powder patterns obtained from monoclinic material (top) and quenched orthorhombic (bottom) TNT samples. Regions enclosed within the dotted lines contain the major differences between the two crystalline forms

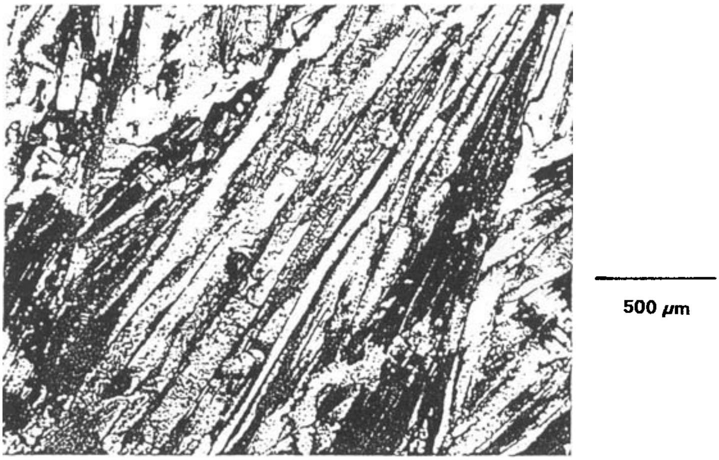

FIGURE 4
Optical Microscopy of Pure TNT sample Slowly Cooled from 85°C (x50)

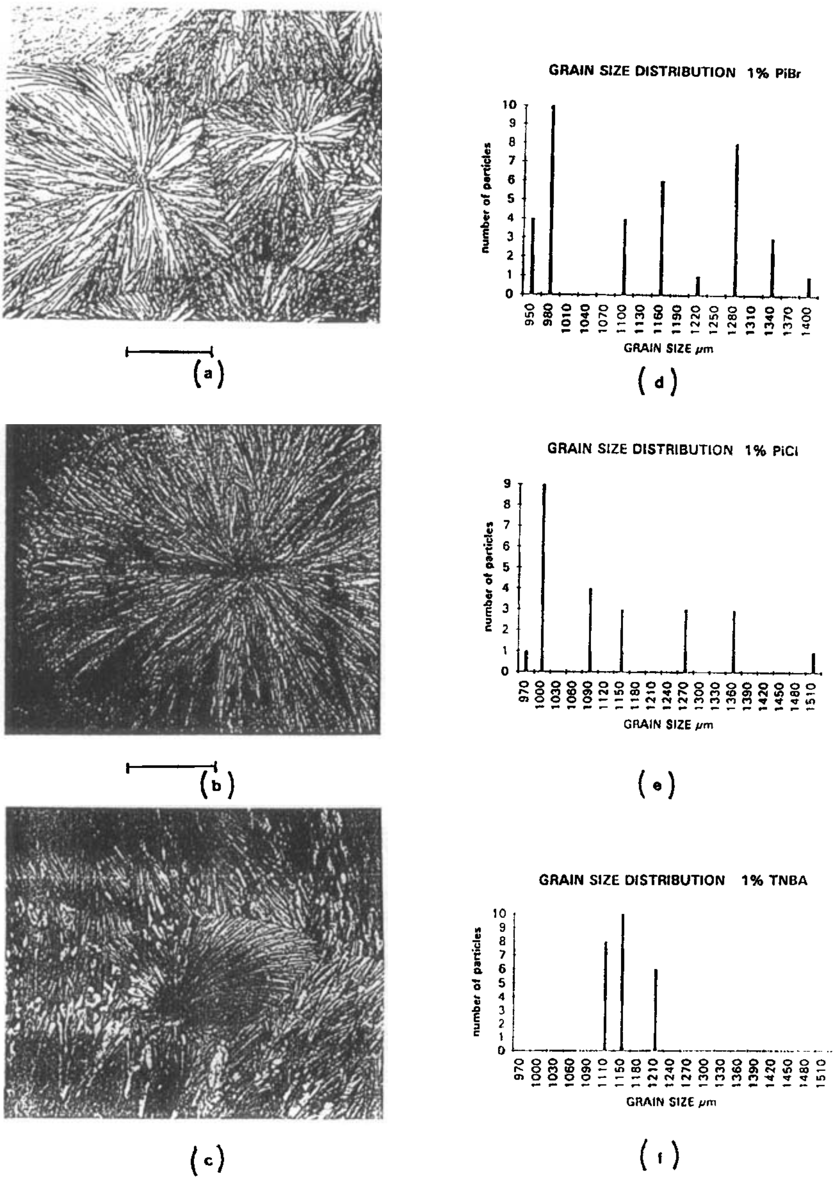

FIGURE 5
Optical Microscopy (a),(b)&(c) and grain size histograms (d),(e)&(f) for TNT treated with 1% PiBr, PiCl and TNBA. Histograms show number of grains with a mean grain size. All recorded at x 50 magnification.

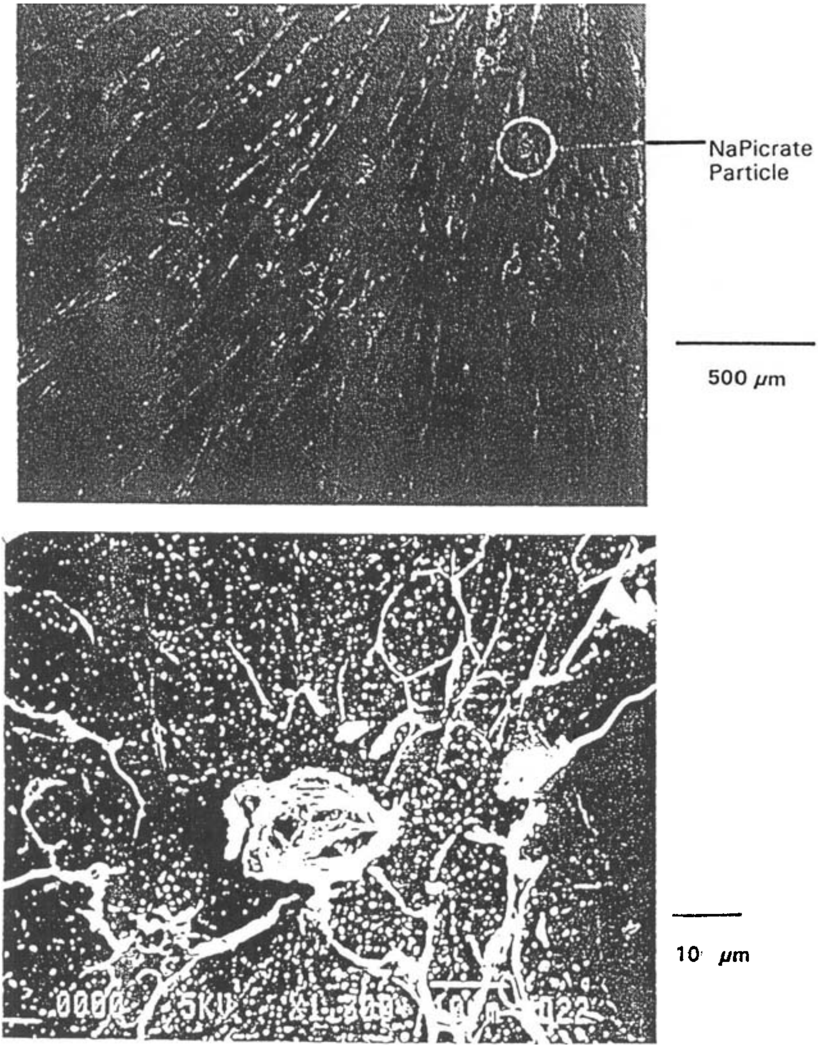

FIGURE 6
(a) Microscope photograph of 1% Sodium Picrate additive crystals and (b) XRF image, using the sodium wavelength, in region of highlighted particle

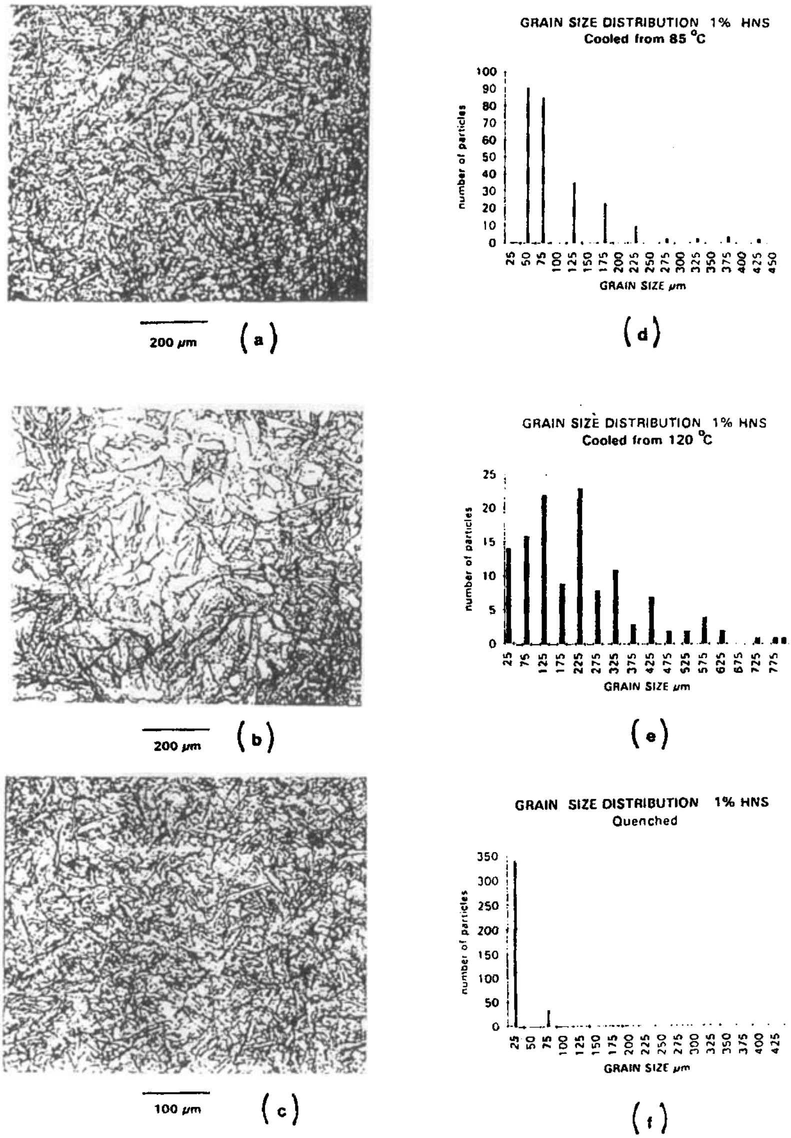

FIGURE 7

Particle sizes of HNS treated samples of TNT produced by (d) slow cooling form 85 ^{O}C (e) slow cooling from 120 ^{O}C and (f) quenching from 85 ^{O}C with the corresponding microscope image photographs (a)-(c). Magnification x 100. Scale marks indicate 200 μm (a) and (b) and 100 μm (c)

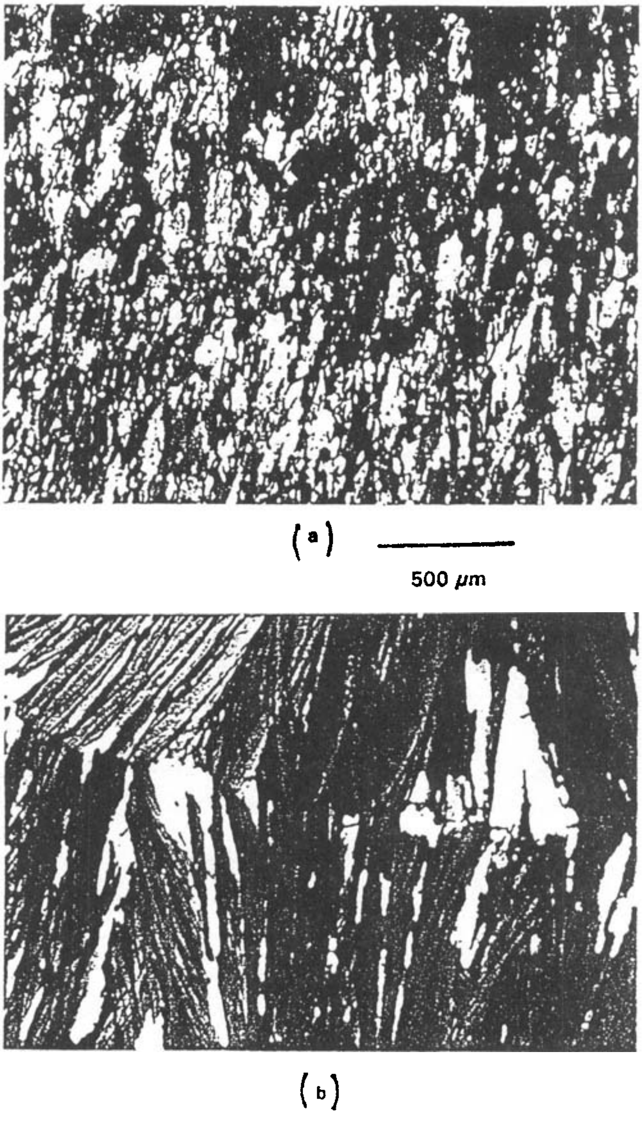

FIGURE 8
Effect of Ultrasound on the setting of pure TNT from 85 ^{O}C (a) with a comparison control sample (b). Scale marks are included

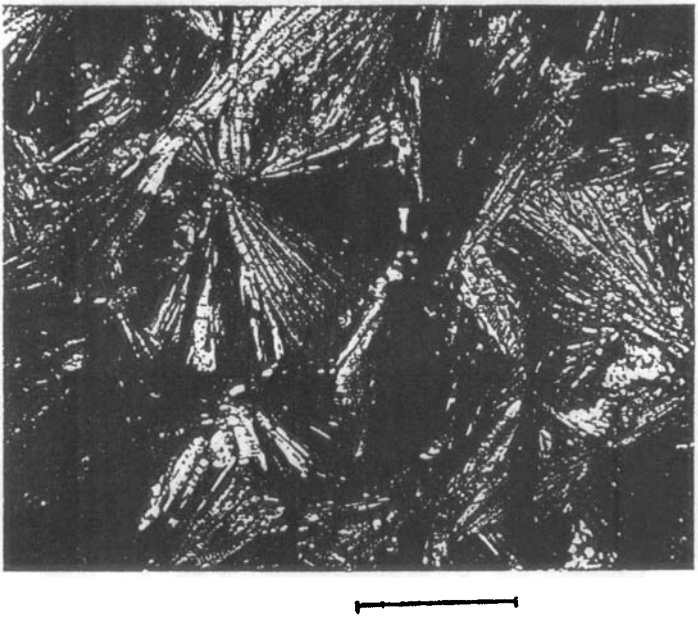

FIGURE 9
Photograph of TNT particles produced by the cooling of large grain, 0.5 - 0.05 mm, HNS samples from 85^{o}C.

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