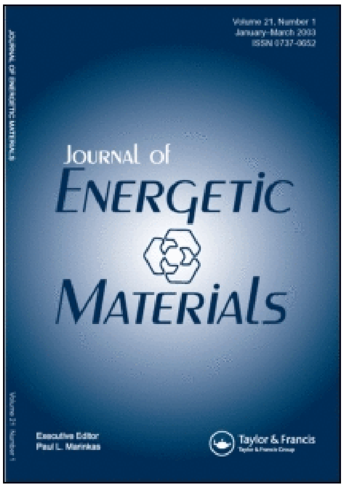

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The Properties of Ammonium Dinitramine (ADN): Part 2: Melt Casting

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A melt casting technique for ammonium dinitramine (ADN) and ADN/aluminum was developed. ADN proved relatively easy to cast, when 1% of magnesium oxide was used as a stabilizer and crystallization kernels. Densities of ADN/MgO 99/1 were 92 to 97% of theoretical mean density (TMD) and those of ADN/Al/MgO 64/35/1 were between 95 and 99% of TMD. Sedimentation of Al in the melt was prevented and the particle wetting was ensured by selecting a suitable particle size for Al. No gelling agents or other additives were used. The casting process and factors influencing it are discussed.

Keywords: aluminum, ADN, mechanical properties, melt casting, metallized explosive

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Background

Ammonium dinitramine (ADN) is an energetic oxidizer that has many uses. One potential application is a melt-castable (underwater) explosive, especially in combination with active metals such as aluminum or magnesium. Because ADN is energetic as such and it consists of only gaseous, low-molecular-weight elements, it enables access to more powerful underwater explosives than previously known. Because no halogen species are involved with ADN it has been called a "green" oxidizer compared to the widely used ammonium perchlorate.

Previously only little has been published [1–3] on melt casting ADN alone or in admixture with other components. So far, ADN has been mainly applied to composite propellants [4–13], which could also be used as an explosive in analogy to present formulations based on ammonium perchlorate, Al, 1,3,5-trinitro-1,3,5-triazine (RDX), and hydroxyl terminated polybutadiene (HTPB) for underwater explosives. However, such formulations require extensive processing and control of many factors such as particle size distribution, crystal morphology, viscosity of the polymer, compatibility, aging, etc. The detonation properties of melt-cast ADN have been published and investigated in admixtures with nano-diamonds and nano-aluminum powders [2,14], but the process of casting ADN has not been hitherto described in detail.

In this article, the properties of molten ADN are discussed and a method for casting ADN with and without aluminum powder as an energetic additive are described in detail. Melt casting ADN was expected to solve more problems than it introduces, when compared to formulations containing ADN in a binder matrix. Even though the mechanical properties of a melt-cast explosive are not as good as those of a polymer-bound formulation, the ease of processing outweighs the drawbacks in many cases. Additionally, the highest possible performance out of ADN is available by using it as such with active metals (Al, Mg) as a fuel.

Physical Properties

ADN has a relatively low melting point at 91–93°C and it has a low viscosity in a molten state. Its thermal expansion is

Table 1
Some physical and chemical properties of NEXPLO-manufactured ADN (NEXPLO, Karlskoga, Sweden)

Property	Value and method
Melting point	91–93.5°C (DSC)
Decomposition	150°C (onset) to 230°C (end of exotherm) by DSC
Heat of fusion	130 ± 5 kJ/kg (DSC)
Heat capacity, C_p, solid	1.8 ± 0.2 kJ/kg (DSC)
Coefficient of thermal expansion, volumetric, solid	$1.91 * 10^{-4}$ 1/K (by gas pycnometer)
Density, solid, 25°C	1820 kg/m^3 (X-ray diffraction)
Density, liquid, 100°C	1560 kg/m^3 (pycnometer)
Shrinkage on solidification	14.0%
Moisture content	0.1–0.2% (Karl-Fischer)

relatively high and the expansion is not isotropic but depends on the crystal orientation [15]. Therefore, it is difficult to determine an accurate linear expansion coefficient directly based on the X-ray diffraction measurements and we give only the bulk thermal expansion of volume, which was determined by measuring the density at different temperatures. The expansion in the phase transition liquid–solid is also large. These physical properties of ADN are listed in Table 1. The high volume reduction in liquid- to solid-phase transition indicates that melt casting is prone to building up voids, cracks, and stresses as the material shrinks during solidification. The heat of fusion is also relatively large, which in combination with a low heat conductivity makes it slow to melt down ADN in large amounts. On the other hand, these physical properties are advantageous when molten material is to be transferred and when it solidifies.

Discussion of the Procedure

The physical properties of ADN affect the casting procedure strongly and generate many boundary conditions that have to be taken into account to successfully cast high-density charges out of ADN or its mixtures. These properties of ADN and their influence on the casting procedure are discussed below. Before these details are discussed it is strongly warned that ADN is an explosive material and the reader is advised to carefully read the safety warnings below before proceeding further.

Safety Warning

Although we experienced no problems with melt casting of ADN, all explosive materials in general and the procedure described in this article are inherently dangerous. This is especially true with ADN, which requires more stringent safety precautions than applied normally in similar work. All work in larger than gram scale must be carried out with remotely controlled equipment such as utilized in this work while taking proper precautions, including planned standardized operations and experienced personnel. Though ADN is difficult to detonate, has relatively large critical diameter (40 mm), and requires a large booster to be ignited, it deflagrates violently due to its exceptionally high linear burning rate compared to more commonly used energetic materials such as RDX, 2,4,6-trinitrotoulene (TNT), or ammonium perchlorate-based compositions. In addition, ADN ignites more easily than common energetic materials due to its relatively low decomposition temperature (150°C). In a powdered state with a high surface area the material may cause explosions due to self-confinement, if ignited in any larger amounts than a few tens of grams. Because of this, the melting equipment should not be a closed even with a light cover, because an explosion is very likely to result, if ADN is ignited in even a semi-closed vessel. In practice this means that conventional TNT-melting kettles are unsuitable for casting ADN. All vessels must be as open and flat as possible to prevent any pressure buildup and only the required amount of ADN should be molten at one time.

Any combustible material mixed with ADN will further enhance its burn rate and the potential hazard associated with an accidental ignition. Molten ADN without a stabilizer is unstable and prolonged heating may cause an ignition due to autocatalytic decomposition as also shown by the microcalorimetry experiments [15]. Even with a stabilizer, the time in the molten state must be minimized to prevent all of the stabilizer being consumed before the material has solidified again. The temperature control in the entire procedure must be exceptionally rigorous and no point of the equipment may exceed 100°C or a risk of an accidental ignition becomes too high. Because the melting point of ADN is 91–93°C, this leaves only a very narrow safety margin, which must be taken into account when planning for the procedure.

Compatibility

The greatest safety concern with ADN is its incompatibility with many common materials as well as impurities. Thus, the melting equipment must be rigorously cleaned before working with ADN, which may come into contact with fully compatible materials only. ADN is very reactive with most materials, which either react with ADN or catalyze the decomposition of ADN or both. Some compatible materials include stainless steel (SS2343, V4A, AISI316), aluminum, magnesium, gold, polytetrafluoroethylene (PTFE), perfluorinated rubber (Viton), polyethylene without dyestuffs, RDX, HMX, zinc oxide, magnesium oxide, Dow Sylgard 170 two-component silicone resin, and Plexiglas (as thoroughly cured polymer only). On the other hand, common materials like rust, iron, nickel, copper and its alloys and compounds, silver and its alloys and compounds, cyanoacrylate glue, and polyacetal (Delrin) are totally incompatible with ADN and will cause an autoignition of ADN within minutes to hours. Molten ADN can ignite spontaneously upon contact with these materials. Every material involved in working with ADN must have successfully undergone a full set of compatibility tests before it can be safely brought into a contact with ADN.

Small Charges and Preliminary Experiments

Small charges out of pure ADN (from NEXPLO, Karlskoga, Sweden), ADN/MgO, and ADN/Al/MgO were both pressed and cast and the densities measured (Table 2). The charges were first

Table 2
Densities of pressed and cast ADN

Sample	Density (kg/m^3)	% of TMD
Pure ADN, cast, ambient pressure	1660	92
Pure ADN, vacuum cast	1640	90
ADN/MgO 99/1, cast, ambient pressure	1760	97
ADN/MgO 99/1, vacuum cast	1740	95
Pure ADN, pressed, 80 MPa, 25 mm diameter	1580	87
Pure ADN, pressed, 80 MPa, 40 mm diameter	1660	92
Pure ADN, pressed, 90 MPa, 10 mm diameter	1670	93
ADN/Al/MgO 64/35/1, cast, vacuum	1960	95
ADN/Al/MgO 64/35/1, cast, ambient pressure	2050	99

manufactured to 25+ mm in diameter and 25+ mm in length. Thereafter, they were turned in a remotely controlled lathe to 25.00 ± 0.01 mm diameter and 25.00 ± 0.01 mm length in order to measure the volume with high precision. A gas pycnometer or weighing in a fluid could not be used, because the fluid would enter the pores left by the casting, giving too high a density.

ADN was pressed with and without additives. Densities varied between 87 and 97% of theoretical mean density (TMD) depending on the method used. Axial one-sided pressing without a vacuum resulted in the lowest density and double-sided axial pressing under vacuum produced the highest density of the pressed pellet, as would be expected. Previously, densities up to 95% of TMD have been obtained by pressing [16].

Casting Pure ADN. Gas Generation

It was found that pure ADN both as such and in admixture with Al cannot be melt cast due to excessive gas generation, whereas ADN can be easily pressed to relatively high density without any additives. The gas evolution in pure molten ADN results from decomposition reactions, which make it even more undesirable and dangerous, especially if the process is scaled up. On the other hand, castings with MgO as a stabilizer produced castings with nearly theoretical densities. There was some gas evolution with MgO-stabilized ADN as well, but in this case the gas was ammonia released from ADN by the basic material MgO according to the reaction:

$$\mathrm{MgO} + 2\mathrm{NH_4N(NO_2)_2} \rightarrow \mathrm{Mg(N(NO_2)_2)_2} + 2\mathrm{NH_3} + \mathrm{H_2O}$$

The gas generation from MgO-stabilized ADN was not dangerous as such but it is still advisable to minimize it to avoid gas bubbles in the castings, to prevent too much water from forming during the process, and, above all, to make sure that all the MgO is not consumed before the ADN has solidified. It was also checked that the gas from MgO-stabilized ADN melt was indeed ammonia, which results from the reaction of MgO with ADN (reaction above). Because water is also formed in the reaction, the reaction accelerates with time and the gas generation rate increases the longer the material is kept molten. Water works as a solvent, making the reacting species more mobile and the reactions become faster due to faster mass transfer. The ammonia generation is not harmful from the safety point of view because magnesium dinitramine is a stable compound, but if all the MgO is consumed before ADN solidifies there is concern regarding whether the ADN casting remains stable long-term afterwards, because the effect of magnesium dinitramide as a stabilizer has not been investigated. Attempts to introduce a vacuum to remove the gas bubbles from the melt only caused the gas generation to be accelerated or at least the bubbles grew significantly due to the reduced pressure and the achieved densities were very poor, often under 60% of TMD.

The gas generation can be best avoided by using as low a casting temperature and keeping the time in the melt as short as possible. It was found that the temperature should not exceed 100°C at any location or the gas generation increases rapidly. At 110°C there is a high risk of an autocatalytic decomposition and a subsequent ignition, although the ignition temperature of ADN is 150°C by differential scanning calorimetry (DSC). This narrow allowable temperature range sets stringent requirements for the equipment and to the procedure and poses risks that must be taken into account already at the planning stage. No additives were used to lower the melting point, because the material was desired to be as pure as possible for characterizing the detonation properties of ADN. In addition, mixing anything into ADN always necessitates a complete compatibility study of the material in question, which was not possible in the scope of this work for all materials of interest.

Large Charges

The casting procedure was scaled up to 5-kg charges. There are a number of factors to take into account when scaling up, mostly connected with the physical properties of ADN. They are discussed separately below.

Heat of Fusion and Heat Capacity

ADN has a relatively high heat of fusion (130 kJ/kg), which makes ADN slow to melt down. The heat capacity (1.77 kJ/(kg K)) is also very high compared to most other melt-castable explosives. Because the maximum allowable temperature is only a few degrees above the melting point of ADN, efficient heat transfer from the melting vessel to the material needs to be ensured in order to melt the material within a reasonable time. We found that it was not possible to melt more than 1 kg in a 15-L rotating vessel or the melting time was extended too much, leading to heating periods over an hour and giving rise to more gas evolution than desired. As a comparison, up to 5–8 kg of TNT can be melted within an hour with the same equipment.

The problems above arise from the small allowable temperature difference between the melting vessel and the melt, because one cannot exceed 100°C at any location of the kettle either. This leaves only 7–9°C difference between the vessel wall and the melting point of and, in contrast to almost 20°C for TNT under the same conditions. Temperatures higher than 100°C reduced the density of the casting by 5% of the TMD for each degree of centigrade exceeding 100°C. Any lower than the optimal temperature would extend the melting time and the time in a molten state too much and would also reduce the density of the casting due to excessive generation of ammonia. In addition, the high heat of fusion requires large amounts of energy to be transferred into the materials, which further slows down the melting process.

Thermal Stability

The thermal stability of ADN has been measured with DSC (10°C/min) and microcalorimetry [3]. The decomposition starts at 150°C (onset) in DSC and continues up to about 230°C (end of exotherm). In the microcalorimeter the decomposition becomes autocatalytic in 4 h without stabilizers and in 2 days with MgO at 95°C. Other stabilizers we have investigated so far are less effective; however, recently new stabilizers for ADN have been developed [17]. It has also been shown that materials promoting hydrogen bonding in the solid phase stabilize ADN [18], which partly explains why magnesium oxide is effective as an ADN stabilizer. Small amounts of water in ADN also stabilize it, which further explains why it is not advisable to use anhydrous and [19–21]. In addition, casting ADN successfully requires MgO or another kernel builder for optimal crystal growth as well, which the organic stabilizers do not provide and a combination of both may or may not be effective in stabilizing ADN better than MgO alone.

Frothing

The gas evolution causes ADN to froth and some foam will be collected on the surface (Fig 1). This porous part has to be cut away after the charge has solidified (Fig. 2). If the charge is very long, there may not be enough time for the bubbles to rise to the surface, density gradients may remain in the material,

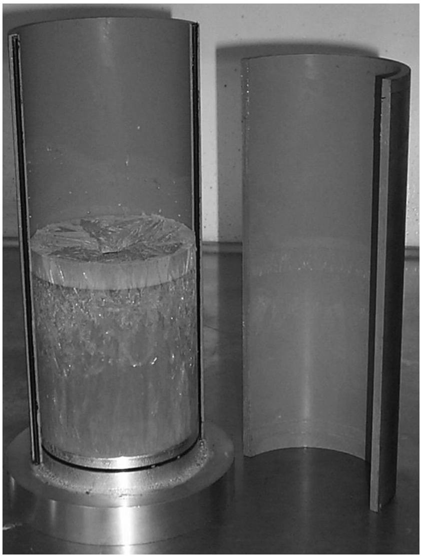

Figure 1. One hundred twenty-millimeter casting form with a solid block of ADN/Al. The separate layer on the top of the block is frothed, very low-density material due to ammonia release from ADN + MgO.

and an undesirably low density is obtained at the upper part of the material. Therefore, the gas generation limits the maximum length of charges that can be cast. Charges up to 300-mm length were cast without problems, but this is getting close to the practical upper limit. Longer charges than that could not be tested, because the available forms were only 350 mm long. When a 300 mm long and 120 mm diameter charge was cast, 60 to 120 mm had to be cut off from the top of the block to remove the foam and the funnel-shaped recess formed during the solidification of the material. This is less than with TNT, which easily develops much larger crystals and voids at the surface and a longer funnel as well. In TNT castings, similar voids are formed and they usually extend deeper than a depth equalling one charge diameter showing that ADN behaves well despite its high shrinkage on solidification. This is probably

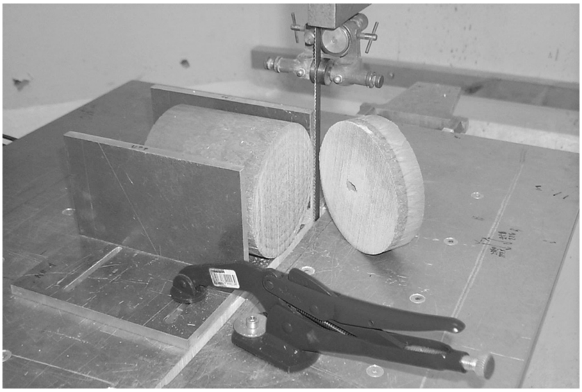

Figure 2. Porous ADN collected at the surface and sawed off. The caliper gap is 100 mm. A cavity caused by shrinkage can be seen at the sawed surface on the front side of the ADN piece and the extremely porous structure is also visible. The entire block weighs less than 200 g despite its size. WARNING: All mechanical processing of explosives is dangerous and must be carried out with remotely controlled equipment, like the bandsaw shown in this picture, behind a safety wall. The saw cutting speed must be kept under 20 m/min, the blade must be new, sharp, free of rust, well cooled with pressurized air, and it must not tend to run askew, causing excessive friction and heating of the ADN block. No cooling liquids are allowed with ADN, because they may dissolve ADN or be incompatible with it. All dust must be immediately removed by suction using an anti-static pipeline, vacuum equipment, and a dust bag, all consisting of ADN-compatible materials. The dust must be destroyed immediately after the procedure has been completed, because it may contain impurities that catalyze the decomposition of ADN.

due to the high heat of fusion of ADN, which helps to slow down the solidification process and allow time for the molten material to fill any voids formed. In addition, the directional solidification procedure used helps to reduce the lost head volume.

The foamy surface reduces the funnel length by isolating the surface thermally and by supplying the solidifying ADN with more material from the top to fill in the forming cavity, but at the same time it also insulates any heat from possible exothermic reactions in the melt. At first we thought the foam collecting at the surface was not desirable and removed it as soon as it formed. This caused the ADN to start crystallizing at the surface, because it was exposed to the ambient air, despite putting an insulating polyethylene foam lid on top of the form. Having ADN crystallize on the free surface caused a deep and irregularly shaped cavity to form, which was filled with loose needle-like crystalline mass. When the foam was left intact, not touched in any way to break or disturb it, the cavity at the top was only half the depth compared to the one formed when removing the foam and contained very few loose crystals. Moreover, the foam contains much less wasted material than a solid mass of crystals with voids, like one formed in TNT castings, and less high-density material had to be cut away after the block had solidified. Thus, the gas generation is not a totally negative phenomenon as long as the gas does not originate from the decomposition of ADN but is ammonia released from the ADN-MgO reaction. Gas generation cannot be fully avoided, because either the stabilizer reacts with ADN releasing ammonia, or without stabilizers dangerous decomposition reactions take place, leading to even more gassing.

Solidification Rate and Freezing Process

Surprisingly, we found that the density increased the faster the ADN was solidified, which is an opposite behavior to many other materials. We believe the effect is based on finer crystals formed in a rapid solidification. If ADN has time to crystallize as large crystals, shrinkage will cause the bulk material to crack at crystal boundaries, creating air-filled voids, which reduce the bulk density. This happens because the bonding between crystals in ADN is relatively weak. If the material is frozen fast, the smaller crystals formed distribute the stresses more evenly and the material is less likely to crack. By letting the material solidify axially and as fast as possible, less radial stresses are formed because the material solidifies as an axial front. If the process is slow, thermal losses to the environment through the form walls cause the material to start freezing at the walls and the solidification front runs in a radial direction causing radial stresses.

Another reason for better density is probably the shorter time available for decomposition and gas generation, even though any trapped gas has less time to escape from the melt. The gas inclusion process is also dependent on the layer thickness. Because we did the cooling experiments in relatively small scale (10–100 g), bubbles could escape quickly and very good results were obtained. Thicker layers would probably show a density gradient with a higher density at the bottom and lower on the top of the casting, if they could be cooled as fast as the small test charges. Consequently, an optimal cooling rate should be tested for each charge size to be cast.

Fine crystalline material did not show a tendency to cracking like the coarse crystalline materials did. Hence, it is generally best to freeze molten ADN in the form as fast as possible, ensuring that a central cavity does not form. Ideally, the solidification should be axial; i.e., begin at the bottom and proceed through the material as a front. This ensures that all gas bubbles will have maximal time to rise onto the surface before the material freezes and traps them and that the central cavity is kept as small as possible, because there is molten material available from above to fill it if such a cavity should form due to material shrinkage.

Shrinkage

ADN shrinks by 14% of its volume upon solidification. This gives rise to the formation of a large cavity in the center of the castings, where the material solidifies last, and to high internal tensions and a tendency to form cracks in the solid material. Cavities are unacceptable in most cases and it becomes necessary to control the cooling process more accurately than is necessary with TNT-based castings. In practice, a molten layer of ADN has to be present on top of the solid material during the entire solidification process to prevent any cavities from forming and the material must solidify axially.

We accomplished the above by placing a heating mantle around the tubular forms we used (Fig. 3). The mantle was heated up to 105°C and lifted slowly during the solidification process to make the ADN solidify as a front and minimize any cavities. This method proved very successful and the final cavity depth at the top in a finished 300-mm-long casting was less than half the diameter of the block. Without a heating mantle, the cavity extended down to three quarters of the charge length or even through it and contained 10–12% of the entire block volume. Thus, the cavity becomes almost as large as the shrinkage of the material upon solidification unless directional freezing is used. The directionally frozen samples had less than 4% of total volume in the conical recess at their surface, but this recess often contained a porous network of needle-like crystals, between which some additional empty volume was present. The volume of this porous mass was not determined, but it might well account for another 1–2% of the block bulk volume. Despite the cavity volume, the material loss accounted for less than 10% of the total charge weight, which was considered good enough and the procedure was not optimized further.

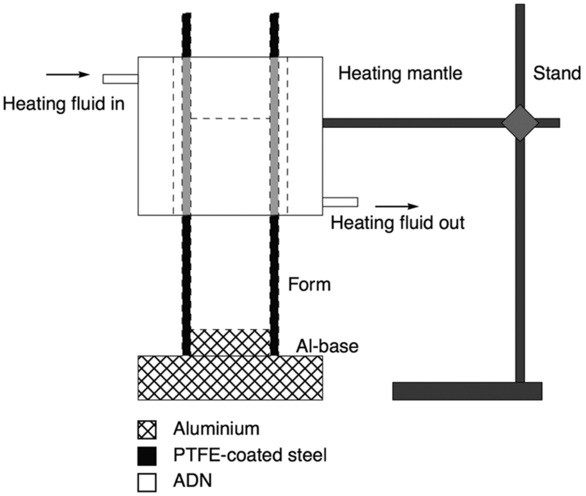

Figure 3. A schematic view of the ADN casting equipment.

Thermal Conductivity

ADN appears to have a low thermal conductivity. Unfortunately, we were unable to measure it and a quantitative value cannot be given. We found that it is difficult to cast very large diameter charges (>150 mm), because the center takes too long to solidify and gas evolution may become a problem. Dipped heaters in the center of the charge were not successful in solving the problem either. The heater easily gets stuck in the material because only a very thin layer of ADN stays molten around it, and the rest is solid. Instead, external heating of the form or thermal insulation has to be utilized in order to restrict the cooling to a desired location of the form only.

Moisture

The ADN as received contains 0.1–0.2% of water. At first it was thought that this water should be removed prior to casting and the castings should be kept in a desiccator to prevent them from absorbing more water from the air. This assumption proved wrong. ADN directly from a manufacturer's container resulted in higher densities than very dry ADN. In addition, keeping the castings in a dry environment caused them to crack and erode mechanically. Chips of ADN started falling off the surface spontaneously, large cracks developed, and it was even possible to hear a fizzling and crackling sound when the block of ADN kept breaking down under high mechanical tensions caused by the shrinkage of the casting. This caused some concern regarding the stability of ADN at first until the cause for this phenomenon was investigated in detail. Having a 1/10% of moisture in ADN made it mechanically completely stable and blocks of such material could be machined like TNT or 60/40 RDX/TNT, to which the mechanical properties of ADN are similar. Blocks of ADN can be handled like any block of explosive, but care has to be taken not to expose ADN to direct sunlight or moisture due to its high hygroscopicity and sensitivity to ultraviolet radiation. If a block was allowed to stand in ambient air at 50% relative humidity for a few hours, it would become deliquescent on the surface due to absorbed moisture dissolving ADN.

ADN and Aluminum

Molten ADN has a very high surface tension, which sets some limits for possible aluminum powders that can be mixed with it. In addition, ADN is a very polar molecule, which effectively removes the possibility of using grease or wax-coated metal powders. Surface active agents could not be used to facilitate wetting of the metal particles and more homogeneous mixing because of compatibility of such materials with ADN. Several different types of aluminum powders were tried and it was found that spherical and smooth particles produce the best density and homogeneity of the castings at approximately 10 µm size, whereas irregular particles have an optimum average particle size at 50 µm. A 3-µm Al powder (Valimet H-3, Valimet Inc., Stockton, CA) could not be mixed with molten ADN at all but would only float on top of the melt, regardless of whether the powder had been premixed with powdered, crystalline ADN. This was obviously a wetting problem with the small particles. A 10-µm powder of the same type (Valimet H-10) was easy to mix in and caused no such wetting problems.

At the coarse end, a 100-µm powder (Carlfors A-80, Carlfors, Huskvarna, Sweden) quickly sedimented onto the bottom of the melting pot as well as the casting form. Thus, it was not possible to use such a coarse powder without some thickeners in the ADN melt, which again could not be employed because of unknown compatibility with the ADN. A 50-µm, irregularly shaped Al-powder (Carlfors A-100) was found to perform very well and produced the highest densities in the finished castings. This powder was also easiest to handle and mix into ADN melts, in addition to being the best available material from a local manufacturer. This particular 50-µm powder was finally selected for all larger charges to be cast.

A 10-µm irregularly shaped powder (Mepura 10 µm, MEPURA Metallpulvergesellschaft, Ranshofen, Austria) was also mixed well, but the viscosity of the mixture became so high it would not even flow out of the melting kettle under its own weight. The density of the casting with this powder was very poor, only 50% of theoretical, probably due to trapped air.

It was concluded that the best Al powder particle size range is 10 to 50 µm. The best particle shape was found to be irregular, because such particles do not sediment in the casting form as fast as spherical particles do, despite being larger. However, spherical Al is also perfectly usable, if the particle size is small enough to prevent sedimentation before the melt solidifies but large enough to ensure a thorough wetting of the metal particles by the molten ADN.

Casting Procedure—General

ADN and ADN/Al mixtures were melted in a stainless steel rotating kettle and thermostated to no more than 100°C (Fig. 4). The exact temperature at the surface of the kettle interior was not measured, but it was between 108°C (heating

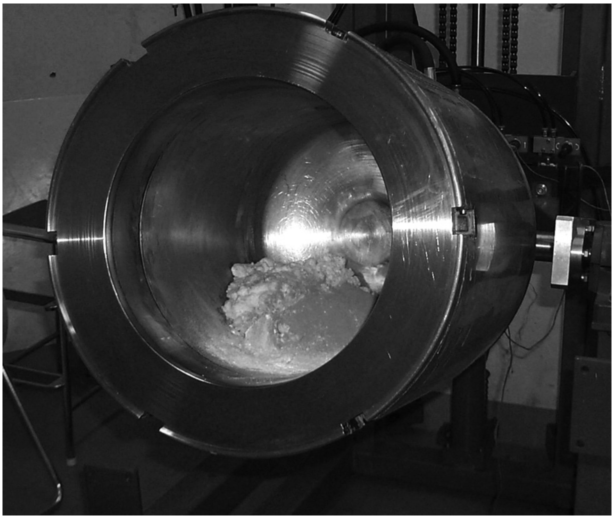

Figure 4. Melting kettle used for casting ADN loaded with ADN/Al/MgO charge ready to be melted and cast. The kettle rotates around its longitudinal axis and is heated with heating fluid circulating inside the double-walled structure. When all material has melted and the rotation has been stopped, the kettle is tilted and the melt is poured into the form assembled at correct position below the vessel mouth.

fluid in) and 90°C (heating fluid out). The required heating fluid inlet temperature was determined experimentally starting with 100°C at the inlet. This temperature was not enough to melt the ADN in the kettle. The temperature was then raised by 1°C and the new temperature was kept constant, until the returning flow temperature also stabilized to a constant value, which took 15 to 20 min. This procedure was continued until the ADN in the kettle started melting. At this point the inlet temperature was 103°C. Next, the inlet temperature was raised in 1°C steps to heat the molten ADN above the melting point to allow some working time after pouring and not have the ADN freeze immediately on contact with the form and to accelerate the melting itself. Inlet temperatures up to 113°C were tested with small 100-g charges to minimize the time in the melt and the time to melt the ADN. Each charge was cast into a small block, which was machined clean and the density was determined. The optimum temperature was found to be 108°C and this value at the inlet produced the best quality of the castings and the highest densities.

The forms were manufactured out of steel coated with PTFE, which was carefully inspected to be intact and free of cracks or any holes in order to prevent ADN from contacting the bare steel. The form itself was a tube, which can be split into two halves to remove the cast block and there was a Viton O-ring (Trelleborg AB, Trelleborg, Sweden) band attached between the halves as a seal (Fig. 1). An aluminum ring was turned and fitted on the top to hold the halves together and a stainless steel hose crimper was placed at the lower part to tighten the assembly. An aluminum plug was machined and a Viton O-ring fitted to it as a seal. The plug worked both as a plug and as a stand to hold the form in an upright position on the table as well as a heat sink to generate a crystallization front in the melt. A heating mantle around the form was manufactured of aluminum and fitted with heating fluid circulation. The mantle was attached to a stand that allowed shifting it up and down (Fig. 3).

The complete casting form with its bottom plate installed were placed into an oven and heated up to 100°C prior to pouring the molten ADN into the form. Next, the form assembly was quickly wrapped with thermal insulation, transferred to the foundry room, and ADN was poured in as quickly as possible to prevent premature freezing. It should be noted here that ADN could not be overheated as much as TNT to prevent premature freezing due to the lower thermal stability of molten ADN. The safe working temperature range with molten ADN is only within the limits 93 to 100°C, which poses a challenge in transferring the material from the melting pot to the form and not having it freeze on its way.

The form was then transferred onto a table and the bottom block was placed onto another, larger, cold aluminum block in order to quickly initiate the solidification process from the bottom. As molten ADN tends to supercool, it is imperative to initiate the solidification as quickly as possible in a controlled manner or the melt might start crystallizing at random locations or overall at the same time, resulting in a poor-quality casting with cracks and voids. The heating mantle was lowered to expose one third of the form length at the bottom and allowed to stand there for 10 min. After that, the mantle was lifted up 3 cm every 5 min, until it reached the height of four fifths of the form length. At this point, the oil circulation was closed and the entire system was left to stand until it had cooled down to below the ADN melting point. Finally, the form was removed from the mantle, opened, and a solid bar of ADN was obtained.

The bar was then cut with a remotely controlled band saw into two approximately 100-mm pieces, which were turned with a remotely controlled lathe to the desired diameter and length. An air-cooled cutting piece without any cutting fluid was used, because such fluids might dissolve the ADN and might not be compatible with it. The finished blocks were removed from the lathe chuck quickly to prevent them from gathering moisture from the air, which was moistened to above 50% relative humidity (RH) to eliminate static discharges. This is not ideal with ADN, which becomes deliquescent at 50% RH and above; however, we were not able to dry the air below this limit because of both safety and regulatory reasons. The bulk density of the finished blocks was determined by weighing the blocks and measuring their dimensions by a digital caliper with 0.01-mm precision.

Experimental

A typical procedure is described for casting charges from 1 to 5 kg out of ADN-aluminum mixtures or ADN alone. In case of ADN alone the aluminum powder is simply left out of the procedure described below, but the 1% of magnesium oxide can never be omitted or ignition may occur. Charges larger than 5 kg can be cast with the same procedure, but a larger melting kettle than the one used in this work is needed to facilitate faster heat transfer into the material.

A 102-mm-diameter by 350-mm-length tubular casting form was thoroughly cleaned, dried, and assembled. The form, including the bottom block made of aluminum, was placed into an oven heated to 100°C. The thermostat for the heating mantle oil circulation was turned on and set to 105°C.

A 40-L rotating stainless steel melting kettle was preheated up to 85–90°C by setting the inlet temperature to 100°C and waiting until the return flow temperature had stabilized. This procedure took 45 min if starting from room temperature. Thirty-five grams of finely powdered magnesium oxide free of agglomerates was placed into the kettle followed by 1,225 grams of Carlfors Bruk A100 aluminum powder (Carlfors Bruk, Huskvarna, Sweden) (average particle size 50 µm). On top of these materials, 2,240 g of ADN was placed and the materials were gently mixed with a stainless steel spatula. The kettle rotation (45 rpm) was started and the heat fluid circulating thermostat was set to 108°C. The process was followed through a video camera and the rotation was stopped when all the ADN had melted and the mass had become homogeneous, 25–30 min after setting the thermostat to 108°C. The casting form was removed from the oven and quickly wrapped in polyethylene foam insulation. The form was transferred to the foundry room, the kettle was tilted using a hydraulic tilting mechanism, and the molten ADN/Al/MgO mixture was poured within 10–15 s into the form. The residual material adhering to the walls of the kettle was scraped free with an electrically conducting polyethylene scraper and also transferred into the casting form. The form was transferred onto a table and placed on a 50-mm-thick,

300×300 mm aluminum block. The insulation was removed and the heating mantle was lowered on the form so that one third of the form length at the bottom was left exposed. The form was left standing for 10 min, after which the heating mantle was raised 30 mm every 5 min. When four fifths of the casting form was exposed, the heating mantle thermostat was turned off and the entire assembly was left to cool for 2–3 h. The form assembly was carefully opened and the block of ADN/Al/MgO 64/35/1 was removed. All parts and the melting kettle were washed with distilled water and wiped dry with pure cellulose tissue paper. All residual materials and the contaminated tissue papers were immediately destroyed by burning using a remote ignition from a safe distance.

The block was transferred to a remotely operated band saw equipped with a new and sharp cutting band. The cutting speed was adjusted to 20 m/min and the feeding rate to less than 10 mm/min. The block was then clamped into position and the cut was placed approximately 10 mm below the foamy interface, which was clearly visible as a sharp line between lighter and darker material (Fig. 1). The band saw was started and the lost head was cut off with remote guidance through a video camera. The clean block was transferred to a remotely controlled lathe and the end faces were turned parallel and the diameter was turned to 100 mm. The residual materials from the band saw cutting and the powdered residue from the lathe were immediately destroyed by burning using a remote electrical ignition from a safe distance. The finished block was stored in an electrically conductive airtight polyethylene bag to avoid picking up moisture from the air until assembled into a Plexiglas tube and fixed into position with Sylgard 170 two-component silicone resin for a detonation parameter study.

Results

Several blocks of ADN and ADN/Al in various sizes were cast for detonation velocity and radius of curvature measurements (Figs. 1, 2, and 5). The final length for all blocks was 200 mm. The blocks were cast longer than needed in order to cut off the

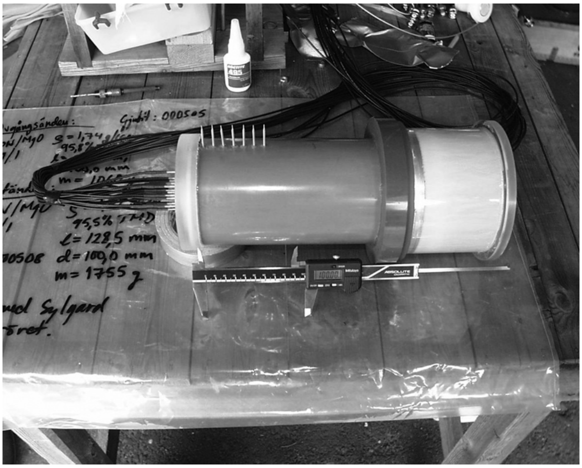

Figure 5. Finished 100-mm charge of ADN/MgO 99/1. The charge is initiated with a 120-mm plane wave lens at the right end. At the left end, piezoelectric pins are installed to measure the radius of curvature; at the side, similar pins are used to record detonation velocity. The ADN is enclosed in a polyvinyl chloride (PVC) tube to protect it from moisture and secured in place with Dow Sylgard 170 two-component silicone, which also isolates the ADN from contact with the PVC and ambient moisture.

foam and the cavity formed on the top of the casting and to obtain the desired length of void free material. The excess length was chosen to be equal to one charge diameter to ensure no defects would remain within the finished block. This provided enough margin in all cases and did not waste any more material than was necessary. In addition, the leftover blocks could be remelted and recast to the next charge, which was done with the largest ones in order to conserve ADN.

Final diameters for the charges were 25, 40, 60, 100, and 120 mm. The charges were cast in the next available form size, which were 26, 44, 66, 102, and 125 mm in diameter. The 120-mm-diameter block was cast in two 150-mm-long pieces and the excess was sawed off, because the form available was not long enough to cast the required 300-mm-long bar in one run. All the other sizes were cast in a single run.

Conclusions

We found that ADN can be melt cast easily, but the technique for melt casting TNT cannot be directly applied. Unstabilized ADN cannot be melt cast due to excessive gas generation rate and risk of initiation.

ADN has a low coefficient of thermal conductivity, which limits the size of the charges to be cast due to gas evolution from the melted substance. Charges up to 100 mm diameter and 300 mm length were successfully cast; hence, the maximum dimensions of a cast ADN charge are at least this large.

ADN shrinks more than TNT while solidifying, making it more difficult to obtain a void-, crack-, and tension-free casting. An embedded heater in the middle of the cast form, as is customary when casting TNT, cannot be used but the forms have to be heated externally and solidification has to take place axially.

Cast ADN has a higher density than pressed ADN, in contrast to TNT-based compositions. ADN must contain some moisture to make it melt-castable and mechanically stable. ADN that is too dry will crumble to pieces by itself after a few days of storage.

Aluminum powder can be mixed into ADN at least up to 35% content without problems; in fact, Al mixtures are easier to cast than ADN without Al with the correct type of aluminum powder. The optimal aluminum powder particle size is 10 μm for spherical and smooth particles and 50 μm for irregularly shaped powder. ADN with aluminum shows significantly better mechanical properties than pure ADN. ADN with aluminum produces the same or better quality of casting as with pure ADN; i.e., the relative density as percentage of TMD is the same or higher with aluminized ADN. Aluminum functions as crystallizing kernels for ADN, producing much finer crystalline material than ADN without Al. MgO is an effective stabilizer for ADN and it also works as crystal nucleation kernels in molten ADN during solidification. The highest density of the cast ADN or ADN/Al is obtained when the material is solidified as an axial front and as fast as possible starting from the bottom of the form.

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