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AN EVALUATION OF ETHYLENE-VINYL ACETATE COPOLYMERS AS DESENSITIZERS FOR RDX IN INSENSITIVE BOOSTER COMPOSITIONS PREPARED BY THE SLURRY COATING TECHNIQUE

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ABSTRACT

Twelve ethylene-vinyl acetate (EVA) copolymers with vinyl acetate contents ranging from 12 to 51% have been evaluated as desensitizers for RDX, for production of insensitive booster compositions. The RDX/EVA compositions were prepared by a solvent-slurry coating process, in which a solution of the EVA copolymer in a suitable solvent is added to an aqueous suspension of RDX, the solvent then being removed by distillation to effect coating of the polymer on the RDX. The efficiency with which the EVA copolymers coat the RDX crystal surfaces increases with increasing vinyl acetate content, and can be altered by the use of surfactants.

The RDX/EVA compositions all have excellent thermal stability, as assessed by the vacuum thermal stability test. The shock sensitivities of compositions prepared with copolymers containing 28 to 51% vinyl acetate were found to be between those of tetryl and PBXW-7, with the shock sensitivity generally decreasing with increasing vinyl acetate content. In general, the EVA coatings gave little desensitization to impact or cookoff; only one composition had a figure of insensitiveness (F of I) which meets current impact sensitiveness requirements for booster explosives for fuzes, and only two compositions gave mild reactions in small-scale cookoff tests. It is unlikely that an insensitive booster explosive composition containing only RDX with an EVA coating could be developed; however, further work on systems using EVA copolymers with additional materials should be undertaken to further examine desensitization mechanisms and identify formulations which may produce insensitive booster compositions.

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AN EVALUATION OF ETHYLENE-VINYL ACETATE COPOLYMERS AS DESENSITIZERS FOR RDX IN INSENSITIVE BOOSTER COMPOSITIONS PREPARED BY THE SLURRY COATING TECHNIQUE

1. INTRODUCTION

1.1 Insensitive Booster Compositions

Australian produced ordnance usually contains tetryl in the fuzing and TNT- based melt-cast compositions as the main charge filling. While these compositions have been adequate for most applications it is quite clear that alternative polymer bonded explosive (PBX) compositions developed overseas are considerably less vulnerable to many hazardous stimuli and can offer several other significant advantages such as enhanced underwater performance.

Currently two cast-cured PBX compositions are being evaluated at MRL as main charge fillings in Australian ordnance. PBXN-107 (formerly PBXC-116) [1,2] is an alternative to TNT-based melt-cast compositions for use in both medium and large calibre shell and aircraft-carried ordnance, where its higher maximum operating temperature (greater than 100°C) makes it suitable for deployment on aircraft in environments where extreme aerodynamic heating may occur [3]. PBXW-115 is more powerful and less vulnerable than the TNT-based compositions which have traditionally been used in Australian naval mines and related stores, and is under assessment as a replacement for these fillings [4]. Munitions containing both PBX compositions have low vulnerability to bullet/fragment impact, do not undergo sympathetic detonation, and also give mild responses under fast cookoff conditions, i.e. when ordnance containing the compositions is heated in fuel fires. However, to fully realise these benefits it is essential that the explosive composition used in the fuzing for this ordnance is also insensitive to these stimuli. One of the major concerns is cookoff behaviour; violent response of the booster, even non-detonative, could give sufficient shock stimulus to any unconsumed main charge for a shock to detonation transition to occur [5]. Alternatively the hot, high velocity fragments from a violent explosion in the booster assembly could initiate the main charge [6].

There has been considerable research and development in the UK and US directed towards the preparation of insensitive booster compositions. However, the problem has not been satisfactorily resolved; currently no insensitive booster compositions are qualified. For proper fuze function it is essential that these compositions are more sensitive to detonative stimuli than the main charge. Therefore they often contain a nitramine high explosive (RDX or HMX) which may be blended with a more thermally stable and less sensitive high explosive (e.g. TATB). A polymeric binder is incorporated to give the required mechanical properties to the booster charge. The binder may have a pronounced effect on the sensitivity of the composition to shock, mechanical/bullet impact [7, 8, 9], hot fragments [10] and cookoff [6, 10], and must therefore be chosen with care.

Fluorocarbon polymers exhibit very good thermal stability and have been used in several insensitive booster compositions [11] including the US Navy's PBXW-7, Type II (RDX/TATB/Viton A 35:60:5) [12] and the BX compositions (RDX/HMX/TATB/PTFE) [5] developed in the UK. However, there is poor adhesion between fluorocarbon polymers and the sensitive nitramine [13] and the coating efficiency is usually poor [14, 15]. The resulting moulding granules can be quite sensitive to impact because of air entrapment between the explosive crystals and the polymer film [14]. Furthermore the poor coating efficiency militates against good cookoff behaviour. It has been shown that effective polymer coatings on explosive crystals undergo minimal disruption during pressing and help confer good cookoff behaviour on the pressed charges [6]. This arises because a well spread, adherent coating disperses the growing shock wave in the run-up preventing a deflagration to detonation transition [6].

Polyethylene wax (PE) is another binder used to prepare booster compositions [16, 17], however it is unlikely to coat explosive crystals well enough to be used in insensitive booster compositions. In Composition A/PE it gave a granular, porous, non-adherent coating on the RDX crystals and the cookoff behaviour was very poor [6]. In contrast copolymers of ethylene and vinyl acetate can give good coatings on RDX crystals [6] and have excellent surface adhesion [13, 18]. The polar vinyl acetate groups wet the surfaces of the RDX crystals and adhesion is enhanced by Lewis base - Lewis acid interactions between the ester groups of the copolymer and the nitro groups of the explosive [18]. These compositions have extremely mild cookoff responses when good coating efficiencies are achieved [6]. It has been suggested that this favourable behaviour is enhanced because the binder undergoes an endothermic decomposition at temperatures close to the exotherm for the decomposition of RDX [18] and thus helps suppress the runaway thermal decomposition reactions of the explosive.

Ethylene-vinyl acetate (EVA) copolymers give moulding granules with other desirable properties which make them well suited for incorporation in insensitive booster compositions to be used in Australia. To obtain charges of sufficient quality it is often necessary to hot press insensitive PBX compositions. However, if EVA copolymers with low glass transition temperatures (Tg) are used the compositions can be cold pressed, making production pelletting operations much simpler. The ethylene content also assists in the pressing operation by providing added lubrication. The resultant pressed pellets are cohesively strong and can be temperature cycled without cracking [18].

At the commencement of this study it was not clear how the properties of various commercially available EVA copolymers would affect the preparation, processing and sensitivity of booster compositions containing RDX. Furthermore, these compositions are prepared by the slurry technique [19-21] which has been widely used in the US but differs substantially from techniques currently used for coating explosives in Australia. Therefore it was also necessary to gain local expertise with this technique. Accordingly the first stage in developing an insensitive booster composition for use in Australia involved a thorough evaluation of a range of EVA copolymers to identify those most appropriate for this application. Concurrently it was necessary to develop an effective method for coating these polymers on RDX crystals.

1.2 Ethylene-Vinyl Acetate Copolymers

The physical properties of the range of commercially available EVA copolymers are quite varied. They are largely determined by the vinyl acetate content when the molecular weights are sufficiently high (chain lengths greater than 1000 vinyl monomer units) [22]. The copolymers evaluated in this study generally have shorter chains and their properties are also influenced by the molecular weight and the molecular weight distribution, which both show a strong dependence on the polymerization technique used and the reaction conditions [23].

Ethylene and vinyl acetate are commercially polymerized at relatively high pressures by bulk, solution, suspension or emulsion techniques. Both monomers have almost equal reactivities at pressures above 100 MPa (1000 atm) and copolymers of a random type are formed under these conditions. At lower pressures vinyl acetate is more reactive and the copolymer initially formed will contain a higher percentage of this unit. A more uniform polymer is obtained under these conditions by continuous feeding of this monomer to the reaction medium at the appropriate rate [24]. Side reactions in the homopolymerization of ethylene [25] and vinyl acetate [26] introduce some chain branching. The level of long chain branching observed in polyethylene is similar to that found in the EVA copolymers when both types of polymer are produced by the high pressure process [22].

Polyethylene produced at high pressures is partially crystalline and partially amorphous. The crystallinity results from close packing of polymer chains, with very long sequences of ethylene groups, into layers (or lamella). The polymer chains have lengths of about 100 carbon atoms between folds. Branching occurs in the homopolymer and this disrupts the crystalline structure, thus introducing amorphous segments and lowering the density of the polymer. Polyethylene with a density of 0.92 Mg/m^3 is approximately 50% crystalline and has a crystalline melting point of over 110°C [27]. No major glass transitions have been observed over temperatures ranging down to -40°C although a number of secondary glass transitions have been observed [27, 28]. The polymer is ductile well below 0°C, has a medium-to-high stiffness [27] and a moderately high tensile strength.

The incorporation of vinyl acetate comonomer into the ethylene backbone of the polymer further reduces the crystallinity of the polymer. Each acetate side group prevents four carbon atoms on each side of it from entering polyethylene crystals. Thus as the vinyl acetate content is increased up to 45 weight %*

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* Vinyl acetate content in EVA copolymers can be expressed as either weight % or mole %. The former term will be used throughout this report, abbreviated as %.

(approximately 25 mole %) the crystallinity falls to zero. The vinyl acetate groups therefore have a plasticising effect on the polymer because they reduce the crystallinity. This effect is enhanced because they also increase the distance between the polymer chains. The change in crystallinity directly affects many physical properties. The melting points, tensile yield strength, hardness and stiffness are reduced [22]. EVA copolymers with low vinyl acetate contents (10-30%) are thermoplastic but similar to semi-crystalline polyethylene. As the vinyl acetate content increases the polymers become more flexible, softer and extensible. They have mechanical properties similar to natural rubber and develop large stresses at long elongations. Copolymers with 50-70% vinyl acetate are amorphous rubbers with high elongation but low tensile strength. At these compositions the stiffness of the EVA copolymers reaches a broad minimum [24]. The glass transition temperatures of the copolymers gradually increase to approximately -40°C at 50% vinyl acetate [27].

When the vinyl acetate content is 75% the copolymer is equimolar. Copolymers containing 80% vinyl acetate are soft, waxy, tacky materials with very low tensile strength [23]. Further increase in vinyl acetate content leads to more numerous polar interactions between the polymer chains causing a reduction in flexibility [26] and higher cohesive and tensile strengths [29]. Flexibility is also reduced because ethylene units in the copolymer are free from steric hindrance and their replacement by vinyl acetate groups introduces more impediment to free rotation about the carbon-carbon backbone of the polymer and reduced intra-chain mobility [26]. The stiffness and glass transition temperature of the copolymers also increases and their properties approach that of pure polyvinyl acetate, which is hard and amorphous with a glass transition temperature of approximately 30°C and a low softening point [24].

The binder for an explosive composition should neither melt nor become brittle during exposure to climatic extremes. It is desirable that the binder have a melting point of greater than 70°C and a low glass transition temperature. These requirements preclude the use of copolymers with very high vinyl acetate contents.

Commercial copolymers with varying molecular weights and vinyl acetate contents of 12 to 51% were selected for evaluation. The properties of copolymers within this range seemed most appropriate for cold pressing, desensitizing the explosive and preparing cookoff resistant compositions. Cookoff behaviour might be expected to be influenced by the vinyl acetate content of the copolymer. The endothermic decomposition of these copolymers occurs at temperatures above 200°C and involves elimination of acetoxy groups via six membered transition states to give acetic acid and unsaturated sites [23, 30]. Copolymers with higher vinyl acetate contents might remove more heat from the exothermic decomposition of the explosive and reduce the likelihood of a violent response. Possible correlations between vinyl acetate contents and cookoff behaviour were therefore examined in this report.

1.3 The Slurry Technique

PBX moulding powders for pressed booster compositions are usually prepared by the slurry technique [19-21]. The polymer used is a solid resin that is dissolved in a suitable organic solvent which is immiscible with water, has a high vapour pressure and does not dissolve the explosive used. The polymer solution is added to an agitated aqueous slurry of the explosive and is required to wet the explosive crystals by displacing water. The mixture is then heated and the solvent is removed by distillation or vacuum air sweep to effect deposition of a polymer coating on the crystals' surfaces. During this process the polymer coatings contain residual solvent and are tacky. The coated particles agglomerate into beads. When most of the solvent is removed the mixture is cooled and the moulding granules are collected by filtration and dried.

Three variations on this method have also been occasionally used. In the reverse slurry process [31, 32], the explosive crystals are stirred with the solution of the polymer in organic solvent then this slurry is added to agitated water and the solvent is removed by heating the mixture. The starved addition technique [33, 34] involves very slow addition of a dilute polymer solution to a very dilute agitated slurry of the explosive in water, followed by heating the mixture to remove the solvent. Using this technique the polymer can be applied in a comparatively uniform film to the explosive at very low levels (less than 0.5% w/w on the explosive). Crystals which are individually, but not completely, coated with polymer can be produced. A subsequent prilling step, involving softening the polymer coating with solvent to achieve controlled agglomeration, can lead to spherical particles with enhanced bulk density. These heavier particles can overcome electrostatic forces more easily and flow well in automatic pelleting machines. The starved addition technique is only suitable for the production of very small batches of explosive moulding powders because of the need to operate with very dilute aqueous slurries of the explosive. Finally the normal slurry technique can be altered to approximate starved addition by dropwise addition of the polymer solution to an aqueous slurry of the explosive heated just above the boiling point of the solvent or its azeotrope with water [35]. The polymer coating is gradually deposited and the continuous removal of the added solvent reduces the tackiness of the polymer coating and the agglomeration.

Several factors influencing the coating efficiency and granule size obtained by the slurry technique have been discussed by Worley [33]. Polymers with a molecular weight of at least 10,000 usually give the best results. High solubility in the organic solvent is important and usually is observed with amorphous rather than more ordered crystalline polymers. The polymer solution must have a low contact angle with the explosive to achieve sufficiently high wettability and solvents with low surface tensions are often used. The solution must also be low enough in viscosity to readily flow around the crystals prior to solvent removal. However, if the viscosity is too low the solution can be easily sheared off the crystal surfaces leading to thin coatings of inferior quality [36].

A protective colloid, typically polyvinyl alcohol, is often added to prevent flocculation and stabilize the emulsion formed between the polymer solution and water. Droplets of the solution are deposited on the crystal surfaces during the process and flow together to form the coating. Some surfactants facilitate this process and also help stabilize the emulsion. If the concentration of the protective colloid is too high, poor coating results because the polymer droplets are too well stabilized and do not coalesce on the crystal surfaces [14]. Surfactants and colloid stabilizers can be used to control agglomeration and thus the flow properties of the final product [14, 15]. Granule size can also be altered by varying the water to solvent ratio, the degree of agitation [37] and the temperature of the heated slurry. At elevated temperatures some polymers can become soft and tacky, resulting in clumping of the polymer coated crystals [33].

Clearly a detailed study of this technique with RDX and EVA copolymers was necessary to find conditions which gave the desired granule size and optimized the polymer coating efficiency to improve cookoff behaviour.

2. EXPERIMENTAL APPROACH

A number of compositions with a nominal ratio of RDX to EVA copolymer of 95:5 were prepared by the slurry technique to determine:

(i) the effect of the vinyl acetate content and properties of the EVA copolymer on the properties of the final moulding granules and compacted charges,

(ii) the best method of slurry coating to achieve optimal coating of the copolymer on the explosive crystals, and

(iii) the effect of the copolymer composition and coating efficiency on the cookoff behaviour of the compacted moulding granules.

Moulding granules were prepared by a general slurry coating method using twelve EVA copolymers with vinyl acetate contents of 12 to 51% and a range of properties (Table 1). The coating efficiencies, impact sensitiveness and vacuum thermal stabilities of all these compositions were compared and the shock sensitivities of compositions prepared from copolymers with vinyl acetate contents ranging from 28-51% were determined.

A parametric study of the slurry coating method was conducted to determine the best conditions for achieving high coating efficiencies and reduced impact sensitiveness for these compositions. This involved studying the effects of the ratio of water and solvent to RDX, additives (polyvinyl alcohol and surfactants) and the mode of addition of the polymer solution on these properties of the moulding granules.

The cookoff behaviour of compositions made using EVA copolymers with a range of vinyl acetate contents and one composition made using Viton A were compared and the effect of improved coating efficiency on cookoff behaviour of some RDX/EVA compositions was assessed.

The data from the above studies were used to identify the best EVA copolymer and coating conditions for preparing insensitive booster compositions.

3. EXPERIMENTAL

3.1 Materials

RDX Grade A, Class 1 (recrystallised) from Albion Explosives Factory was used to prepare all the compositions described in this report. The RDX/Elvax 210 (95:5) composition was also prepared for cookoff testing using RDX [illegible] Class 5 from Royal Ordnance plc, Bridgwater, UK, which is designated as Grade E in this report. These explosives were received wet and were routinely dried at the pump prior to use.

The EVA copolymers examined were selected from the Elvax (Du Pont), Levapren (Bayer) and Vynathene (US Industrial Chemical Co) ranges of products. Viton A, used to prepare RDX/Viton A (95:5), is a vinylidine fluoride/hexafluoropropylene copolymer manufactured by Du Pont.

The following additives were used in the coating experiments:

(i) Mowiol 4-88, a partially saponified polyvinyl alcohol (Hoechst),

(ii) Empilan FD, a non-ionic surfactant (Albright and Wilson Ltd),

(iii) Manoxol OT 60, an anionic surfactant - dioctyl sodium sulphosuccinate (Harcros Industrial Chemicals), and

(iv) Cetyltrimethylammonium bromide, a cationic surfactant (BDH Chemicals Ltd).

All the solvents used were laboratory reagent grade. In all the preparations distilled water was used.

3.2 Slurry Coating Methods

3.2.1 Mixing Equipment

All batches were prepared in an open mixing vessel with a right circular cylindrical shape which was fitted with a heating jacket and two wide baffles perpendicular to the walls of the vessel. The slurries were stirred by an overhead air motor which drove a rod with an impeller at the base equipped with twelve flat blades.

3.2.2 General Method

The following general method was used to prepare compositions from all EVA resins for the comparison of the effect of these copolymers on the properties of the moulding granules and compacted charges. However, when Elvax 210 was used less water (285 mL) was added.

A slurry of RDX (142.5 g) and water (435 mL) was stirred at 500 r/min for 5 min then an aqueous solution of Mowiol 4-88 (0.01% w/w, 15 mL) was added. After a further 10 min a solution of EVA copolymer in toluene (10% w/w, 75 g) was slowly added. The mixture was agitated vigorously for 15 min then it was heated to 60-

65°C. This temperature was maintained until most of the solvent was removed and hard moulding granules had formed. The agitated mixture was cooled to 30°C and the granules were then collected by filtration and washed well with water. In most preparations the oversized granules were separated by sieving the composition under water on a 2.36 mm mesh. The finer granules were dried at the pump and then at 60°C in a vacuum over silica gel.

3.2.3 Parametric Studies on the General Method

Fifty gram batches of these compositions were prepared using Levapren 408 by varying the ratio of water and toluene to RDX, incorporating additives and using an approximation to the starved addition technique. The modifications are detailed in Section 4.2.

3.2.4 RDX/Viton A (95:5)

This composition was prepared by the general method but ethyl acetate was used as the solvent.

3.2.5 RDX/Levapren 408/Zinc Stearate (94:4:2)

An RDX/Levapren 408 (94:4) composition was prepared by modifying the general method and using an anionic surfactant (0.4% w/w on RDX). After the solvent was removed in this preparation the mixture was heated to 85°C and a hot aqueous solution of sodium stearate (5% w/w, 55 g) was added. After 15 min an aqueous zinc sulphate solution (2% w/w, 120 mL) was added at a uniform rate over 30 min and the mixture was cooled. The granules were collected by filtration and dried at the pump and then at 60°C in a vacuum over silica gel.

3.3 Characterization

3.3.1 Scanning Electron Microscopy

Micrographs were obtained using a Cambridge Instruments Model S250 Mk II scanning electron microscope with a tungsten electron gun operated at 15 to 21 kV in the secondary electron mode. The tilt angle used was generally 30 degrees. The samples were mounted using PVA adhesive and sputter coated with a conducting film of gold. Coating efficiencies were usually determined from at least five high resolution micrographs considered to be representative of the composition.

3.3.2 Rotter Impact Sensitiveness : Figure of Insensitiveness (F of I)

A Rotter Apparatus [38] fitted with a 5 kg weight was used to determine impact sensitiveness. F of I values were determined using the Bruceton procedure to analyse results. Unless indicated otherwise these results were obtained using 25 or 50 caps. The values quoted, derived from the height for 50% initiation probability, are relative to RDX Grade F = 80 and are rounded to the nearest five units. Average gas volumes for positive results are also quoted.

3.3.3 Shock Sensitivity : Small Scale Gap Test

Shock sensitivity data was obtained using the MRL small scale gap test (SSGT) [39]. The donor is a UK Mk 3 exploding bridge wire detonator attenuated by brass shim. The acceptor is two 12.7 mm diameter x 12.7 mm height cold pressed cylinders of the explosive under study. A detonation is confirmed using a mild steel witness block. Results were obtained from 20-30 firings using the Bruceton staircase method and are quoted as mm of brass shim for a 50% detonation probability, together with the 95% confidence limits and standard deviation.

3.3.4 Vacuum Thermal Stability Test

This test was carried out in accordance with standard Australian procedures [40]. The results quoted are the average volume (mL) of gas evolved at 120°C over 40 h for duplicate 5 g samples of the RDX/EVA compositions prepared by the general method.

3.3.5 Cookoff Test

The cookoff behaviour of the RDX/EVA compositions and RDX/Viton A was assessed using the Super Small-scale Cookoff Bomb (SSCB) [41, 42] shown in Figure 1. The SSCB uses an explosive sample 16 mm diameter x 64 mm long, with a total mass of approximately 20 g, consisting of four (4) pellets. All the compositions tested were pressed to 90 %TMD. Duplicate tests were conducted on all samples at the fast heating rate, and compositions which showed mild cookoff reactions were subjected to further tests at both fast and slow heating rates. The results presented include the type of cookoff response obtained, and the explosive surface temperature at reaction and time to reaction.

4. RESULTS AND DISCUSSION

4.1 Effect of Different EVA Copolymers on Moulding Granule Properties

All compositions assessed in this section were prepared by the same general method devised in the early stages of studying the slurry coating technique.

4.1.1 Processibility

The slurry coating process produced granules consisting of many partly coated crystals bound together by polymer. Scanning electron micrographs of RDX Grade A and a typical moulding granule are shown in Figure 2 (a) and (b). The different EVA copolymers used to prepare the moulding granules had an effect on granule size, handling properties such as flowability, and the ease of pressing the compositions.

Eight of the compositions produced moulding powders containing large granules, which are unsuitable for pressing. These materials were passed through a 2.36 mm sieve prior to use, and the oversize portions (Table 2) were rejected.

Presumably the copolymers which gave rise to the large granules were those which were most tacky during the coating process and therefore induced most agglomeration [33]. The composition prepared from Vynathene EY 902-35 showed substantial agglomeration (Table 2) and micrographs of compositions containing both Vynathenes showed that polymer films were severely disrupted in these cases (e.g. Figure 3, Micrograph A). This surface disruption may have resulted from intercrystalline contact and subsequent pulling away of the tacky polymer, but could also be a property of these particular polymers.

In contrast, micrographs of most of the other compositions (Figure 3) do not show this type of disruption of the polymer coating. For polymers with approximately the same vinyl acetate content, surface tack should be least for those with the highest molecular weight. If similar branching occurs in these polymers then solution viscosities are an indication of molecular weight. Levapren 400 gives considerably more viscous solutions in toluene (Table 1) than other copolymers with approximately 40% vinyl acetate and does not give rise to oversized agglomerates.

All the compositions prepared in this study were free flowing and when cold pressed they gave acceptable pellets. Some compositions from copolymers with a high vinyl acetate content adhered more strongly to the walls of the mould during pressing and a mould lubricant was required.

The pellets produced for SSCB testing were held in ambient temperature storage for several months prior to and during the testing program. It was noticed that some pellets had grown slightly on storage, and the condition of pellets of different compositions varied. These observations are summarised in Table 3. The pellets produced from all the RDX/EVA compositions showed poorer surface finish than the RDX/Viton A and PBXW-7 pellets.

4.1.2 Coating Efficiencies

All compositions were examined using scanning electron microscopy to qualitatively assess the relative coating efficiencies of the different polymers. Some micrographs of selected compositions are shown in Figure 3, and can be compared with the uncoated RDX Grade A (Figure 2(a)). Only partial polymer coating of the RDX crystals occurred with some bare crystal surfaces exposed in all compositions.

The worst coatings were observed in compositions prepared from Elvax 650 and Elvax 410 which are both copolymers with low vinyl acetate contents (12% and 18%). A typical micrograph (B) of the former composition shows textured polymer deposited on the leading face of the crystal with the surrounding faces uncoated. In both cases the polymer adhered poorly to the crystal surfaces and the moulding granules were easily disrupted revealing that the polymer is largely deposited in coarse polymer strands (Micrograph C) which bind the granule together. The composition containing Elvax 210, which has a vinyl acetate content of 28%, showed an improved polymer coating with the smooth polymer film covering a larger proportion of the crystals' surfaces (Micrograph D). However large areas of uncoated crystal can clearly be distinguished and the overall coating efficiency is only fair.

For the range of compositions studied, a general trend of increasing coating efficiency with increasing vinyl acetate content of the copolymers was observed. This is presumably because copolymer solutions with a high percentage of polar vinyl acetate groups can better wet the surfaces of the RDX crystals. Micrograph E of the composition containing Levapren 500, which has 50% vinyl acetate, illustrates this enhancement in coating efficiency. It shows that a very high percentage of the crystals' surfaces are covered with a smooth polymer film.

In those cases where the copolymers differed only in molecular weight the micrographs revealed that the lower molecular weight polymers generally gave higher coating efficiencies and formed a thinner, more consistent coating film. The lower molecular weight polymers give less viscous solutions in toluene (Table 1) which should flow more effectively across and more completely coat the RDX crystal surfaces. These effects are illustrated in micrographs of Levapren 452 (F) and Levapren 450 (G). The former polymer is lower in molecular weight and gave a high coating efficiency. In contrast micrographs of Levapren 450 revealed inferior coatings and some (e.g. Micrograph G) showed raised areas of polymer which indicated poor flow of the more viscous solution during coating. The coatings obtained using Elvax 40-W did not conform to this general trend. This copolymer has a low molecular weight but gave a significantly worse coating than other copolymers with the same vinyl acetate content.

4.1.3 Impact Sensitiveness

Rotter impact sensitiveness data for the RDX/EVA (95:5) compositions prepared by the general coating method are shown in Table 4, together with data for RDX/Viton A (95:5).

The results show that the most sensitive moulding granules were obtained when the fluorocarbon polymer, Viton A, was used. This confirms the poor desensitization which fluorocarbon polymers may afford [14, 17]. Of the RDX/EVA compositions, only Elvax 210 gave appreciable desensitization; all other EVAs gave compositions of similar sensitiveness to the uncoated RDX Grade A (F of I = 80). The Elvax 210 composition is the only material which meets current impact sensitiveness requirements for booster explosives, i.e. F of I not less than that of tetryl (90) [17].

Both the fracture and thermal properties of polymer additives determine their sensitizing effect on explosives [7, 8]. Some polymers that sensitize do so because they fail catastrophically either by fracture or localized adiabatic shear. This concentrates impact energies in the polymer and can generate hot spot temperatures well in excess of the polymer's softening point [7, 44]. In cases where the polymer deforms in bulk under impact, without localized concentration of energy, the material may reach high temperatures by viscous heating from bulk plastic flow at high strains [5, 45, 46]. The temperature attained will be determined by the thermal properties of the polymer including its latent heat of fusion, specific heat and thermal conductivity which all determine the extent of thermal losses [8, 46, 47]. The specific heats and thermal conductivities of polymers are generally low [8] and so the latent heat of fusion will often determine the final bulk temperature attained. The latent heat of fusion of a polymer depends on the degree of crystallinity and is consequently high for high density polyethylene (63% crystalline, and latent heat of fusion of 115 J g^{-1} [48]). This polymer deforms by plastic flow but has been shown to only reach a low bulk temperature. It has been suggested that the temperature rise is low because of the large energy loss during the phase change [46]. This loss should relieve the energy build up in the sample and may explain the polymer's desensitizing effect on explosives [7, 46].

Copolymers of ethylene with vinyl acetate become increasingly soft and extensible as the vinyl acetate content increases to 50%. If these copolymers behave like polyethylene and deform under impact, the bulk temperature rise in the polymer may be controlled by the heat of fusion associated with melting residual crystalline polyethylene domains. The crystallinity of the copolymers decreases as the vinyl acetate content increases, and they become amorphous at 43% vinyl acetate. Therefore moderation of the temperature rise in the polymer by energy losses associated with melting of the residual crystalline domains will be greater for the copolymers with lower vinyl acetate contents, and they would be expected to give more desensitization than those with high vinyl acetate contents, where higher temperatures may be attained.

Conversely, as the vinyl acetate content increases, the quality of the coating of the copolymer improves (section 4.1.2). This enhanced coating efficiency should lead to greater desensitization [43] by the high vinyl acetate content copolymers, and the poor quality coatings given by the low vinyl acetate copolymers may lead to sensitization by air entrapment between the poorly adhering polymer film and the explosive crystal [14].

These two mechanisms - dependent on coating quality and copolymer crystallinity - act in opposing fashion in their effect on impact sensitiveness as the vinyl acetate content varies. Further work on this subject is presently being undertaken at this laboratory.

4.1.4 Shock Sensitivity (SSGT)

The RDX/EVA (95:5) compositions prepared from copolymers with vinyl acetate contents in the range 28-51% by the general coating method were pressed to approximately 90 %TMD and their shock sensitivities were determined using the MRL small scale gap test (SSGT) [39]. The results obtained are shown in Table 5, and are compared with values obtained for PBXW-7, granular tetryl and a sieve cut of RDX, Grade A.

All the RDX/EVA compositions are more shock sensitive than PBXW-7 and less shock sensitive than tetryl and RDX. The values obtained span quite a wide range of shock sensitivities and the type of EVA copolymer used has a strong influence on the shock sensitivity of the pressed composition. In this case the thermal properties of the copolymers will not be important in determining the sensitivities because the time constraints of thermal transfer processes are long compared with the explosive reaction times in this test [51].

The primary sources of hot spots in compositions of this type are the shock impedance mismatch between the explosive and the binder, and the nature of the voids in the final composition [52]. The shock impedance of the EVA binders should vary with their densities (Table 1) and will therefore be similar for all binders. If the shock impedance mismatch was an important factor then compositions containing copolymers with a higher density, i.e. vinyl acetate content, should be slightly more shock sensitive. The results show that this is generally not the case.

All compositions tested had the same total voidage (10%); however, the size distribution and number of these voids should vary for the compositions and will be determined by the relative degree of flow of the binders during the pressing operation. Binders with a higher degree of plasticity will flow well and many of the smaller voids will coalesce resulting in fewer voids and a greater average volume of each void. The larger voids are less effective at producing chemical reactions than the smaller voids [52] because the shock wave skirts the larger discontinuities while the smaller voids are carried along with it and interact with it more effectively [53]. Therefore the more plastic binders should give less shock sensitive compositions. Plasticity should be greater for soft binders with low elastic moduli and copolymers with higher vinyl acetate contents and lower molecular weights have these properties. These soft, low modulus binders also decrease the shock sensitivity by making the final composition less stiff and susceptible to cracking [54] and less likely to induce reaction growth [55]. These factors may be important in determining shock sensitivities using the MRL small scale gap test because in this test the acceptor is unconfined and rapid quenching of ignition by the rarefaction waves in this test configuration means that these results have a greater reliance on build up than is usual in most gap tests [56].

Another important factor in determining the shock sensitivities of the compositions will be the relative coating efficiencies of the different copolymers on the RDX crystals. Eadie [57] has quantitatively determined the coating efficiencies in various RDX/wax compositions and shown that moulding powders with higher coating efficiencies give pressed compositions which are less shock sensitive. The coating efficiencies in the RDX/EVA compositions increase with the vinyl acetate content of the copolymer and generally appear to be higher for copolymers of a given vinyl acetate level which are lower in molecular weight (Section 4.1.2). Furthermore copolymers with higher vinyl acetate contents would be expected to adhere better to the RDX crystals and these coating films should undergo less disruption during pressing. Thus the combined effects of binder plasticity, coating efficiency and polymer adhesion should all lead to a similar ordering of the shock sensitivities of these compositions. The results in Table 5 generally reflect this ordering. Thus for copolymers from the same supplier that vary only in molecular weight (i.e. Levapren 400 and 408 or Levapren 450 and 452) the copolymer with the lower molecular weight gives the less shock sensitive composition. Copolymers which are higher in vinyl acetate content generally give compositions which are less shock sensitive.

The high shock sensitivity of the composition prepared from Elvax 40-W is not consistent with the general trends in these results. The coating efficiency of this copolymer appears to be inferior to that of other copolymers with the same vinyl acetate content. This may be the major factor contributing to the comparatively high shock sensitivity of this composition.

4.1.5 Vacuum Thermal Stability

Vacuum thermal stability was determined on 5 g samples of the various RDX/EVA (95:5) compositions prepared by the general coating method. The results for these tests conducted at 120°C are shown in Table 6. The usual pass/fail criterion for compatibility with RDX in this test is that the gas evolution should not exceed 5 mL after 40 h at 120°C [58]. Clearly all compositions have extremely low evolved gas volumes indicating excellent compatibility of these binders with RDX.

4.2 A Parametric Study of the Slurry Coating Technique

The general coating method devised in this study involved the use of severe agitation and the addition of a protective colloid (Mowiol 4-88) to limit the size of the explosive moulding granules and thus give compositions suitable for pressing. However, this method resulted in only partial coating of the different copolymers on the RDX crystals (Section 4.1.2). Improved coating efficiency was desirable because it leads to a decrease in impact sensitiveness and a moderation in cookoff response of booster compositions [6]. Therefore, in an effort to optimise coating efficiency, a parametric study of the slurry technique was undertaken.

The majority of these experiments involved the preparation of one composition (RDX/Levapren 408 95:5) on a small scale using variations on the general coating method. The effect of these changes on the type of moulding granules produced and their impact sensitiveness is shown in Table 7. The impact sensitiveness data for the RDX/Levapren 408 composition prepared on a small scale (Entry 1) and a large scale (see Table 4) show that the former composition is less sensitive to impact. Scaling experiments with other compositions gave similar results and this suggests that differences in the degree of agitation between the batch sizes leads to variations in coating efficiencies. Varying other parameters generally produced only minor changes in impact sensitiveness; however, close examination of the various compositions using scanning electron microscopy has indicated that these variations cause clear differences in the nature of the coatings.

4.2.1 Ratio of Water : Toluene : RDX

Increasing the ratio of water to RDX from 3:1 to 5:1 gives a composition which is slightly less sensitive to impact (Table 7, Entry 2) and has a greater distribution of granule sizes. The micrographs of these compositions (Figure 4) show that the polymer film at the exterior of the granules prepared by the general method is textured and appears to be disrupted (Micrograph A). In comparison the composition prepared using more water gives a smoother, more uniform exterior coating on the granules (Micrograph B). With this relatively soft, low molecular weight polymer (Table 1) superior coatings are achieved by the reduction in agitation and decreased frequency of granule collisions which occur when more dilute slurries are used.

In one experiment the volume of toluene used in the coating technique was substantially [illegible]creased but this change did not affect the impact sensitiveness of the product (Table 7, Entry 3).

4.2.2 Polyvinyl Alcohol Additive

Increasing the level of the polyvinyl alcohol (Mowiol 4-88) in the coating mixture to 0.1% w/w on the RDX gave a composition that was tacky and had poor flow properties. In this case the polymer coating on the crystals was less uniform with regions of uncoated RDX clearly visible. This apparent decrease in coating efficiency was accompanied by a small increase in impact sensitiveness of the composition (Table 7, Entry 4). These observations support the conclusion that high concentrations of this protective colloid prevent droplets of polymer solution from coalescing on the crystal surface and result in decreased coating efficiency [14].

4.2.3 Surfactant Additives

A previous study of additives in the slurry coating technique noted that isopropanol acted like a surfactant and resulted in a substantial enhancement of the polymer coating efficiency [34]. When the general method was modified to include this additional solvent a more stable emulsion was formed during processing; however, the product had inferior flow properties and was slightly more sensitive to impact (Table 7, Entry 5). Similarly, nonionic and cationic surfactant additives did not give compositions which were less sensitive to impact. However, all surfactants resulted in smoother, less disrupted polymer coatings and higher levels of an anionic surfactant gave a composition that was significantly less sensitive to impact (F of I = 100). In this case the crystals were well coated with a smooth, improved but incomplete film of the polymer coating (Figure 4, Micrograph C). Unfortunately these granules had poor flow properties and it was necessary to incorporate a second coating of zinc stearate to give a composition (RDX/Levapren 408/zinc stearate 94:4:2, Section 3.2.5) with enhanced coating efficiency for cookoff studies.

The influence of the anionic surfactant (at 0.4% on RDX) on the coating efficiency obtained using Elvax 210 (28% vinyl acetate) was briefly investigated. This additive caused a substantial reduction in the coating efficiency of this copolymer and the solution of the polymer failed to wet the crystal surface, causing the polymer to be deposited in droplets and leaving very large areas of exposed RDX crystal (Figure 4, Micrograph D). Without the anionic surfactant film formation occurred and the coating was superior (Figure 3, Micrograph D). Impact sensitiveness data for the compositions prepared with and without the surfactant (Fs of I of 95 and 130 respectively) show that the former composition, with the inferior coating, is more sensitive to impact. The cookoff behaviour of charges pressed from both compositions is compared in Section 4.3.

4.2.4 Starved Addition

The slow addition of a dilute polymer solution to a heated aqueous slurry of RDX attempted in this study approximated the starved addition technique (Section 1.3) and was expected to result in enhanced coating efficiency. When these conditions were employed the quality of the coating and the impact sensitiveness of the composition were not significantly improved (Table 7, Entry 6).

4.2.5 Other Methods

An alternative confidential method was used to prepare the RDX/Levapren 500 (95:5) composition. This product was less sensitive to impact (F of I = 85) than the RDX/Levapren 500 (95:5) composition prepared by the general method (F of I = 70) (see Table 4). The coating efficiency was also superior.

4.3 Effect of Different EVA Copolymers on the Cookoff Behaviour of the Pressed Charges

The results of SSCB tests on the RDX/EVA compositions at the fast heating rate are shown in Table 8. Also included are results for tetryl, RDX/Viton A 95/5, and PBXW-7 Type II for comparison. Since the violence of cookoff reactions increases with decrease in heating rate [42], only those RDX/EVA compositions which gave mild responses at the fast heating rate were subsequently tested at the slow heating rate. The results for slow heating rate tests are shown in Table 9, again with results for RDX/Viton A 95/5 and PBXW-7 Type II for comparison. Slow heating rate SSCB results for tetryl are not given, since the test results are affected by considerable loss of molten sample prior to reaction [42].

The duplicate tests on all the RDX/EVA compositions at the fast heating rate showed excellent agreement in the type of reaction observed for each composition, although there was often wide variation in the temperature at which reaction occurred, together with corresponding variation in time to reaction. Mild reactions were obtained only with Elvax 210 and Levapren 500; all other copolymers gave detonations or violent explosions. Typical SSCB responses are illustrated in Figure 5.

The results show no correlation between the vinyl acetate content of the copolymer and the type of cookoff response observed. Mild cookoff responses were obtained only with compositions containing Elvax 210 (28% vinyl acetate) and Levapren 500 (50% vinyl acetate). Elvax 210 was the only EVA copolymer which produced a substantial reduction in impact sensitiveness of the RDX/EVA composition; the growth to explosion from hot spots in an impact test or from the external heat source in a cookoff test will involve similar physical processes, and a material which affords desensitisation to impact initiation could be expected to act similarly and reduce the violence of a cookoff reaction.

The coating efficiency has some effect on the cookoff response, but it is not the only factor affecting it. Of the two compositions which gave mild responses, the Levapren 500 had a good quality coating, whereas that of the Elvax 210 was only fair (see section 4.1.2). The copolymers which gave poor coatings all gave violent responses, but some copolymers which gave good coatings also gave violent responses, e.g. Levapren 452. The composition prepared with Elvax 210 using an anionic surfactant, which markedly reduced the coating efficiency (see section 4.2.3), gave a more violent cookoff response.

The overall indication is that materials which can reduce the violence of cookoff reactions show greater reduction at higher coating efficiency, and in this respect confirms the work of Anderson and Pakulak [6] which correlates mild cookoff reactions with complete adherent coatings. Similarly, when Elvax 210 was coated on Grade E RDX, which has a higher specific surface area (smaller particle size) than the Grade A RDX and could therefore be expected to lead to less complete coverage of the crystal surfaces, the cookoff response was again more violent. With Levapren 500, the improvement in coating efficiency given by the alternative method of preparation (which resulted in improved impact sensitiveness (see section 4.2.6)) did not further reduce the violence of the cookoff response from that of the material with a good quality coating produced by the general method (section 4.1.2). Similarly, the improved coating efficiency given when an anionic surfactant was used with Levapren 408 (section 4.2.3) did not bring about a decrease in the violence of the cookoff reaction; detonation was also observed for this material. This behaviour is contrary to expectations based on Anderson and Pakulak's work [6], and indicates that coating efficiency is not the sole factor affecting cookoff response.

There is no correlation between cookoff response and explosive temperature or time to reaction. Although the variation between duplicates is considerable and may overshadow any such trend, mild responses were obtained at the extremes of the temperature and time ranges. This is shown in Figure 6, where the cookoff time and temperature are plotted for mild and violent reactions.

With the exception of Elvax 210 and Levapren 500, the EVA copolymers examined produce no decrease in the violence of the cookoff reaction at the fast heating rate compared to tetryl, the current booster explosive. The fluorocarbon binder Viton A also gives no decrease in the violence of the cookoff reaction. Elvax 210 and Levapren 500 give compositions whose fast cookoff reactions are similar to those of the insensitive US booster composition PBXW-7 Type II.

At the slow heating rate all compositions except PBXW-7 Type II gave violent reactions. One test with the Levapren 500 (with the superior coating given by the alternative coating method) gave only a mild explosion, however a duplicate test produced a detonation.

It should be noted that the mild cookoff responses obtained for PBXW-7 Type II samples in this study should not be taken as an indication that this composition will be a satisfactory cookoff-resistant booster composition. Other results using the same nominal composition (RDX/TATB/Viton A 35:60:5) have shown violent responses at both fast and slow heating rates [41, 42].

The high explosiveness of RDX generally leads to violent cookoff response in compositions containing relatively low levels (up to 5%) of binder/desensitizer [6, 11, 41, 42, 59], and the results of this study confirm this. The current US and UK approach to developing insensitive booster compositions is to incorporate a second insensitive explosive (TATB) in the formulation to modify the cookoff response. Another possible approach may be to incorporate a small amount of a less heat-resistant explosive (e.g. PETN) in order to obtain a mild reaction which will cause charge disruption and release of confinement before the violent RDX cookoff reaction. The EVA copolymers which have afforded a measure of cookoff resistance to RDX alone (i.e. Elvax 210 and Levapren 500) should be considered as binders for further development of insensitive booster compositions utilizing either of these approaches.

5. CONCLUSIONS

A series of RDX/EVA (95:5) compositions has been prepared by a solvent-slurry coating process using ethylene-vinyl acetate copolymers having vinyl acetate contents ranging from 12 to 51%. The efficiency of the copolymers to coat the RDX crystals increases as the vinyl acetate content increases, and decreases as the molecular weight increases. Coating efficiencies are not very sensitive to most changes in experimental conditions; however, an anionic surfactant was found to have a pronounced effect on two of the copolymers, in one case giving a marked improvement in coating quality and in the other a substantial reduction. All the RDX/EVA compositions were found to have excellent vacuum thermal stability.

Only one of the EVA copolymers (Elvax 210) was found to produce a composition which was sufficiently desensitized to impact to qualify for use as a booster explosive. The other EVAs gave little or no desensitisation of the RDX to impact. The effects of both coating efficiencies and copolymer properties, particularly crystallinity, are believed to be important in determining the impact sensitiveness. Further investigation of the impact sensitiveness of these RDX/EVA compositions should be undertaken to establish the relative importance of these parameters and to further elucidate the mechanisms of impact initiation of coated explosives.

The shock sensitivity of pressed pellets of compositions containing copolymers ranging from 28 to 51% vinyl acetate was found to generally decrease as the vinyl acetate content increased; factors determining this trend probably include binder plasticity, coating efficiency and adhesion. All the compositions had shock sensitivities between those of tetryl (the current booster explosive in widespread use) and PBXW-7 (an insensitive US booster formulation).

The cookoff behaviour of the RDX/EVA compositions was assessed using the SSCB test. Only two of the EVA copolymers (Elvax 210 and Levapren 500) gave compositions showing mild cookoff responses at a fast heating rate; however, these compositions gave violent responses (detonations) at slow heating rates. No correlation of the type of cookoff response with vinyl acetate content was observed. The quality of the polymer coating, although important for copolymers which do decrease the violence of the cookoff response, is not solely sufficient to give cookoff insensitive materials. Further studies should be undertaken to establish the relationship between polymer properties and coating efficiencies in their effect on cookoff response.

It is unlikely that an insensitive booster explosive composition containing only RDX with an EVA coating will be attainable. However, some EVA copolymers have shown promise in desensitizing RDX to impact and cookoff. These materials should be considered for use as binders in RDX compositions incorporating a second explosive (e.g. TATB or PETN) to decrease charge hazard response for booster compositions for future insensitive ordnance.

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7. REFERENCES

1. Anderson, C.M. and Pakulak, J.M. (1976). Cook-off studies on the general purpose cast explosives PBXC-116 and PBXC-117 (NWC TP 5629). China Lake, Cal.: Naval Weapons Center.

2. Spear, R.J. (1986). Personal Communication

3. Parry, M.A. and Richardson, D.D. (1986). Personal Communication

4. Parry, M.A. (1987). Personal Communication

5. Hutchinson, C.D. (1985). The thermal response of intermediate explosives to thermal and shock stimuli (PhD Thesis). Cambridge, UK: Cambridge University.

6. Anderson, C.M. and Pakulak, Jr., J.M. (1977/78). Journal of Hazardous Materials, 2, 143.

7. Swallowe, G.M. and Field, J.E. (1982). Proceedings of the Royal Society of London, A379, 389.

8. Swallowe, G.M. and Field, J.E. (1981). Effect of polymers on the drop weight sensitiveness of explosives. 7th Symposium (International) on Detonation, p 13.

9. Wanninger, P. and Kleinschmidt, E. (1987). Pressbare kunststoffgebund sprengstoffe mit hohem fuligrad. ICT Internationale Jahrestagung, Karlsruhe, Germany, p 14-1.

10. Hillstrom, W.W. (1985). Safer explosives with additives. 7th Symposium on Chemical Problems Connected with Stability of Explosives, 149.

11. Kabik, I. and Ringbloom, V.D. (1983). Cook-off resistant booster explosive. US Patent 4,394,197.

12. Baudler, B. and Montesi, L.J. (1986). Qualification test results of PBXW-7 Mod 1 (NSWC/TR-86-22). Silver Spring, MD: Naval Surface Weapons Center.

13. Martin, E.C. and Yee, R.Y. (1984). Effect of surface interactions and mechanical properties of PBXs on explosive sensitivity (NWC-TP-6560). China Lake, CA, USA: Naval Weapons Center.

14. Eerligh, R., van Gool, M.A., Kramer, R.E. and van Ham, N.H.A. (1986). Investigation of the result of coating techniques on high explosives with the aid of scanning electron microscopy/energy-dispersive X-ray spectrometry. ICT Internationale Jahrestagung, Karlsruhe, Germany, p 10-1.

15. Meulerbrugge, J.J., Kramer, R.E. and Leeuwenburgh, A.B. (1987). Investigation into the micro-encapsulation of RDX in viton. ICT Internationale Jahrestagung, Karlsruhe, Germany, p 32-1.

16. Spear, R.J., Nanut, V. and Dagley, I.J. (1986). RDX-polyethylene wax formulations as potential replacements for tetryl in fuze leads, boosters and magazines (MRL Report MRL-R-1015). Maribyrnong, Vic.: Materials Research Laboratory.

17. Spear, R.J., Nanut, V., Redman, L.D. and Dagley, I.J. (1987). Recommended replacements for tetryl in Australian production fuzes and related ordnance (MRL Report MRL-R-1089). Maribyrnong, Vic.: Materials Research Laboratory.

18. Reed, R. and Stanton, H.D. (1978). Mouldable ethylene/vinyl acetate copolymers, US Patent 4,090,894.

19. Dobratz, D.M. and Crawford, P.C. (1985). LLNL explosives handbook (UCRL-52997). Cal. USA: Lawrence Livermore Laboratory, University of California.

20. Wright, S.B. (1965). Granular explosive moulding powder. US Patent 3,173,817.

21. Wright, S.B. (1967). Granular crystalline plastic bonded explosives. US Patent 3,296,041.

22. Salyer, I.O. and Kenyon, A.S. (1971). Journal of Polymer Science, A-1, 9, 3083.

23. Koopmans, R.J., Van der Linden, R. and Vansant, E.F. (1982). Polymer Engineering and Science, 22, 878.

24. Narain, H. and Kapur, S.L. (1979). Ethylene vinylacetate (EVA) copolymers: preparation, properties and applications. Journal of Scientific and Industrial Research, 38, 25.

25. Farmer, D.B. and Edser, M.H. (1983). Chemistry and Industry, 228.

26. Reynolds, C.E.J. (1970). Journal of the Oil and Colour Chemists' Association, 53, 399.

27. Boysen, R.L. (1981). In Kirk-Othmer encyclopedia of chemical technology, 16, 402.

28. Nielsen, L.E. (1960). Journal of Polymer Science, XLII, 357.

29. Reynolds, C.E.J. (1969). British Polymer Journal, 1, 233.

30. Grassie, N. (1952). Transactions of the Faraday Society, 48, 835.

31. Hornig, H.C. and McGuire, R.R. (1980). Preliminary development and characterization of a TATB/HMX plastic bonded explosive (UCID-18534). Cal. USA: Lawrence Livermore Laboratory.

32. Golopol, H.A., Fields, D.B. and Moody, C.L. (1977). New booster explosive LX-15 (RX-28-AS). Livermore, USA: Lawrence Livermore Laboratory.

33. Worley, C.M. (1986). Surface characterization of an energetic material, pentoerythritoltetranitrate (PETN), having a thin coating achieved through a starved addition micro-encapsulation technique (MLM—3348). Miamisburg, Ohio: Monsanto Research Corporation, Mound.

34. Vannet, M.D. and Ball, G.L. (1987). Journal of Energetic Materials, **5**, 35.

35. Konrat, J.P. (1967). Coating of explosives. French Patent 1,469,198 (Chemical Abstracts, **67**, 75040).

36. Thies, C. (1975). Polymer-Plastic Technology and Engineering, **5**, 1.

37. Stull, T.W. (1980). Formulation of custom sized LX-15 granules (MHSMP-80-19). Texas, USA: Mason and Hanger-Silas Mason Co., Inc. Amarillo.

38. Mortlock, H.N. and Wilby, J. (1966). Explosivstoffe, **14**, 49.

39. Wolfson, M.G. (1983). The MRL small scale gap test for the assessment of shock sensitivity of high explosives (MRL Report MRL-R-896). Maribyrnong, Vic: Materials Research Laboratory.

40. Australian Defence Standard (1980). Methods of test for explosives and related materials, DEF (AUST) 5608, Method 3/80.

41. Pakulak, J.M. Jr. and Cragin, S. (1983). Calibration of a super small-scale cookoff bomb (SSCB) for predicting severity of the cookoff reaction (NWC TP 6414). CA, USA: Naval Weapons Center, China Lake.

42. Parker, R.P. (1989). Establishment of a super small-scale cookoff bomb (SSCB) test facility at MRL (MRL Technical Report MRL-TR-89-9). Maribyrnong, Vic.: Materials Research Laboratory.

43. Dagley, I.J., Spear, R.J. and Nanut, V. (1987). High explosive moulding powders from RDX and aqueous polyurethane dispersions (MRL Report MRL-R-1062). Maribyrnong, Vic.: Materials Research Laboratory.

44. Swallowe, G.M., Field, J.E. and Walley, S.M. (1984). Proceedings of 3rd Conference on Mechanical Properties at High Rates of Strain, Institute of Physics Conference Series, **70**, 443.

45. Swallowe, G.M., Field, J.E. and Hutchinson, C.D. (1985). Impact experiments on thin layers of polymers and intermediate explosives. In Y.M. Gupta (Ed.) Shock waves in condensed matter, Plenum Press, N.Y., p 891.

46. Walley, S.M., Field, J.E., Swallowe, G.M. and Mentha, S.N. (1985). The response of various polymers to uniaxial compressive loading at very high rates of strain. Presented at DYMAT '85: International Conference on Mechanical and Physical Behaviour of Materials under Dynamic Loading, Paris, Sept 2-5, publ. les editions de physique.

47. Bowers, R.C., Romans, J.B. and Zisman, W.A. (1973). Industrial Engineering and Chemistry: Product Research and Development, 12, 2.

48. Kamath, P.M. and Wakefield, R.W. (1965). Journal of Applied Polymer Science, 9, 3153.

49. Spear, R.J. and Nanut, V. (1987). Mechanism of and particle size effects on shock sensitivity of heterogenous pressed explosives: preliminary assessment of binderless RDX in fuze trains (MRL Report MRL-R-1077). Maribyrnong, Vic.: Materials Research Laboratory.

50. Spear, R.J. and Nanut, V. (1987). A comparative assessment of US and UK explosives qualified as replacements for tetryl (MRL Report MRL-R-1094). Maribyrnong, Vic.: Materials Research Laboratory.

51. Marshall, W.W. (1970). The role of the matrix in determining the shock initiation characteristics of compositions containing 60% by volume of HMX, 5th Symposium (International) on Detonation, NOL, Pasadena, Cal., 18-21 Aug, p. 124.

52. Cambell, A.W., Davis, W.C., Ramsay, J.B. and Travis, J.R. (1961). Phys. Fluids, 4, 511.

53. Leiber, C.O. (1975). Rheologica Acta, 14, 92.

54. Bower, J.K., Kolb, J.R. and Pruneda, C.O. (1980). Industrial Engineering and Chemistry: Product Research and Development, 19, 326.

55. Fleming, K.A., Bird, R., Burt, M.W.G. and Whatmore, C.E. (1985). 8th Symposium (International) on Detonation, Albuquerque, New Mexico, July 15-19, p 449.

56. Spear, R.J., Nanut, V., Dagley, I.J. and Wilson, W.S. (1988). Anomalous shock sensitivity/density relationship for RDX-polyethylene wax and related formulations from MRL small scale gap test (SSGT) measurements (MRL Report MRL-R-1099). Maribyrnong, Vic.: Materials Research Laboratory.

57 Eadie, J. (1965). The effect of wax on the shock sensitivity of explosive components, 4th Symposium (International) on Detonation, NOL, White Oak, 12-15 October, p 399.

58. Chemical Inspectorate (1965). Compatibility requirements for HR materials. Specification CS 8001, Royal Arsenal, Woolwich, London.

59. Pakulak, J.M., Jr. (1984). USA Small-scale cookoff bomb (SCB) test. Minutes of 21st DoD ESB Explosives Safety Seminar, Houston, TX.

Table 1 Some Properties of the EVA Copolymers

Properties \ Polymer	Elvax 650	Elvax 410	Elvax 350	Elvax 210	Elvax 40-W	Levapren 400	Levapren 408	Vynathene EY 902-35	Levapren 450	Levapren 452	Levapren 500	Vynathene EY 905-00
Vinyl Acetate content (weight %)	12	18	25	28	40	40	40	41	45	45	50	51
Density at 23°C (g/ml)	0.93	0.93	0.95	0.95	0.97		0.96	0.96	0.98	0.98		0.98
Melt Index (g/10 min)	8.5	450-550	19	400	57	2-5	60	70	2	11		18
Softening Point (Ball and Ring) (°C)	150	88	88	62	104		110	110	182	134		121
Hardness Shore A-2 Durometer (10 s)	94	80	70	62	40		32	56	23	30		32
Tensile Strength (MPa)	17	4.7	3.3	2.8	4.8-6.2		3.5	5.5	6.2	5.4		
Elongation at Break (%)	750-850	400-900	600-1000	800-1000	1000-1300		1300	1500	500	900		
Elastic Modulus (MPa)	85	33	16	12.0	3.0							
Viscosity (cps) 20% w/w in toluene at 23°C (Brookfield RVT 2/50)				672	896	1728	864	917	1408	1088	1728	1048

Table 2 **Percentage of RDX/EVA (95:5) Granules Retained on a 2.36 mm Pore Size Sieve**

EVA Copolymer	Percentage retained [a]
Elvax 210	7
Elvax 40-W	12
Levapren 408	5
Vynathene EY 902-35	33
Levapren 450	10
Levapren 452	4
Levapren 500	5
Vynathene EY 905-00	13

[a] Compositions prepared by the general method (Section 3.2.2)

Table 3 **Condition of RDX/EVA (95:5) Pressed Pellets after Ambient Storage for approximately 6 months**

EVA Copolymer	Diameter (mm) [a]	Condition
Elvax 650	16.04	Smooth; shiny sides
Elvax 410	16.12	Smooth sides; slightly rough ends; powdering at edges
Elvax 350	> 16.1 [b]	
Elvax 210	15.94 [c]	Smooth sides; slightly rough ends
	16.04	Slight roughening of all surfaces
Elvax 210AS	16.04	Slightly rough ends; powdering at edges
Elvax 210/ Grade E RDX	15.89 [c]	Smooth; shiny
Elvax 40-W	15.99	Smooth
Levapren 400	16.12	Smooth sides; rough ends
Levapren 408	15.97	Smooth
Vynathene EY 902-35	16.00	Smooth
Levapren 450	16.05	Smooth
Levapren 452	15.93	Smooth; slightly tacky; slight chipping at edges
Levapren 500	15.95	Smooth
Vynathene EY 905-00	16.01	Smooth
RDX/Viton A	15.90	Smooth; shiny
PBXW-7 Type II	15.89	Smooth; shiny

a Pellets were produced using a mould 15.875 mm diameter. Measurements are mean from 4 pellets, each measured at 6 positions.

b Not measured - no pellets remaining; estimated from interference fit in SSCB inner cylinders.

c Pellets were aged < 1 month.

Table 4 **Impact Sensitiveness of RDX/EVA (95:5) and RDX/Viton A (95:5) Moulding Granules**

EVA Copolymer	Vinyl Acetate Content (%)	F of I (a)	Gas Evolution (ml)
Elvax 650	12	75	14
Elvax 410	18	80	10
Elvax 350	25	75	12
Elvax 210	28	130	15
Elvax 40-W	40	85	14
Levapren 400	40	80	16
Levapren 408	40	75	15
Vynathene EY 902-35	41	75	15
Levapren 450	45	70	13
Levapren 452	45	75	14
Levapren 500	50	70	11
(b)		85	9
Vynathene EY 905-00	51	70	15
Viton A	NA	65	14

(a) Relative to RDX Grade F, F of I = 80
(b) Prepared by an alternative (Confidential) method.

Table 5 **Shock Sensitivity (SSGT) of RDX/EVA (95:5) Compositions**

EVA Copolymer	Relative Density % TMD	Shock Sensitivity (mm)[a]		
		$M_{50\%}$	Range $L_{95\%}$	Standard Deviation
Elvax 210	90.00	2.23	2.34 - 2.11	0.054
Elvax 40-W	90.15	2.37	2.40 - 2.33	0.018
Levapren 400	90.05	2.11	2.14 - 2.07	0.016
Levapren 408	90.05	1.85	1.89 - 1.81	0.018
Vynathene EY 902-35	90.00	1.95	2.01 - 1.88	0.030
Levapren 450	90.03	2.13	2.19 - 2.06	0.029
Levapren 452	90.01	1.95	2.00 - 1.90	0.024
Levapren 500	90.03	1.75	1.77 - 1.73	0.009
Levapren 500[b]	90.00	1.79	1.85 - 1.72	0.031
Vynathene EY 905-00	90.04	1.84	1.90 - 1.79	0.026
RDX, Grade A (250-300 μm sieve cut)[c]	90.00	3.360	3.622 - 3.100	0.12
Tetryl, granular[d]	90.0	3.259	3.315 - 3.203	0.021
PBXW-7 Type II[d]	90.0	1.415	1.448 - 1.382	0.015

a All figures are in mm of brass shim
b Composition prepared by an alternative confidential method
c Data from reference 49
d Data from reference 50

Table 6 **Vacuum Thermal Stability Test Results for RDX and Moulding Granules from Various EVA Copolymers**

Composition		Average Gas Volume (mL) Evolved for 5 g of the Composition heated at 120°C for 40 h
RDX Grade A		0.15
RDX/Elvax 650	(95:5)	0.32
RDX/Elvax 410	(95:5)	0.32
RDX/Elvax 350	(95:5)	0.19
RDX/Elvax 210	(95:5)	0.20
RDX/Elvax 40-W	(95:5)	0.09
RDX/Levapren 400	(95:5)	0.07
RDX/Levapren 408	(95:5)	0.32
RDX/Vynathene EY 902-35	(95:5)	0.32
RDX/Levapren 450	(95:5)	-0.02
RDX/Levapren 452	(95:5)	0.29
RDX/Levapren 500	(95:5)	0.06
RDX/Vynathene EY 905-00	(95:5)	0.11

Table 7 **Effects of Varying the General Method for the Preparations of 50 gram Batches of RDX/Levapren 403 (95:5)**

Parameter Varied	Original Value	Altered Value	Impact Sensitiveness (F of I)	Mean Gas Volume (mL)	Comments
1. Mill [a]			80	13	Small, free flowing granules
2. Ratio of Water:RDX	3:1	5:1	95	13	Wide distribution of granule size up to 5 mm diameter
3. Ratio of Toluene:RDX	0.47:1	1:1	80 [b]	12	Small, free flowing granules
4. Percentage of Mowiol on RDX (w/w)	0.001	0.01	80	13	Wide distribution of granule sizes up to 5 mm diameter
	0.001	0.1 [c]	75	14	Small extremely tacky granules, not free flowing
5. Surfactant Type (% w/w on RDX)					
	-	Isopropanol (70)	75	12	Small granules, poor flow
	-	Nonionic (0.1)	80	15	Small, free flowing granules
	-	Cationic (0.1)	60 [b]	10	Small granules, poor flow
	-	Anionic (0.4)	100	12	Small, very tacky granules, not free flowing
6. Starved Addition of Polymer Solution [d]			80	14	

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[a] Method described in Section 3.3.2

[b] Results were obtained using 25 caps

[c] Ratio of water to RDX was 5:1

[d] Ratio of water to RDX (3.5:1), ratio of toluene to RDX (19:1), solvent solution added over 2 h at 87°C

Table 8 **Cookoff Tests (SSCB) of RDX/EVA Compositions. All tests conducted at Fast Heating Rate**

RDX/EVA : 95/5 - EVA Type	Explosive Surface Temperature (°C)	Time (s)	Cookoff Reaction
Elvax 650	252	256	Detonation
	240	259	Explosion (violent)
Elvax 410	271	280	Explosion (violent)
	242	244	Detonation
Elvax 350	250	267	Detonation
Elvax 210 (a)	245	235	Burning (b)
	234	238	Deflagration (c)
	237	246	Explosion (mild)
	242	264	Explosion (mild)
Elvax 210AS (d)	228	250	Detonation
	224	235	Explosion
Elvax 210, Grade E RDX	247	275	Explosion (mild) (b)
	237	244	Detonation
Elvax 40-W	256	276	Detonation
	245	251	Detonation
Levapren 400	247	256	Explosion (c)
	217	260	Detonation
Levapren 408	266	284	Detonation
	230	250	Detonation
Levapren 408 AS/ZnSt (e)	242	265	Detonation
Vynathene EY 902-35	242	268	Detonation
	240	250	Detonation
Levapren 450	271	278	Detonation
	235	248	Detonation
Levapren 452	235	272	Detonation
	242	260	Detonation
Levapren 500	274	293	Deflagration (b)
	240	255	Deflagration (b)
(f)	263	258	Deflagration (c)
(f)	249	253	Deflagration (c)
Vynathene EY 905-00	262	285	Detonation
	261	267	Detonation
RDX/Viton A 95/5 [42]	260	271	Detonation
PBXW-7, Type II [42]	265	266	Burning
Tetryl [42]	257	239	Detonation
	268	240	Detonation

(a) Results from two batches of material.
(b) Appreciable amounts (> 2 g) of unconsumed explosive recovered after test.
(c) Traces of explosive or parts after test.
(d) Material prepared using anionic surfactant.
(e) Material prepared using anionic surfactant, with zinc stearate coating - see Section 3.2.5.
(f) Material prepared by alternative confidential method.

Table 9 **Cookoff Tests (SSCB) of RDX/EVA Compositions. Tests conducted at Slow Heating Rate**

Only those RDX/EVA compositions showing mild responses at the fast heating rate were tested in this series of tests.

RDX/EVA : 95/5 - EVA Type	Explosive Surface Temperature (°C)	Time (s)	Cookoff Reaction
Elvax 210	217	1628	Detonation
	220	1681	Detonation
Elvax 210, Grade E RDX	220	1757	Detonation
Levapren 500	217	1704	Detonation
(a)	217	1592	Explosion (mild) (b)
(a)	217	1659	Detonation
RDX/Viton A 95/5 [42]	217	1577	Detonation
PBXW-7, Type II [42]	213	1657	Deflagration (b)

(a) Material prepared by an alternative confidential method.
(b) Traces of explosive on parts after test.

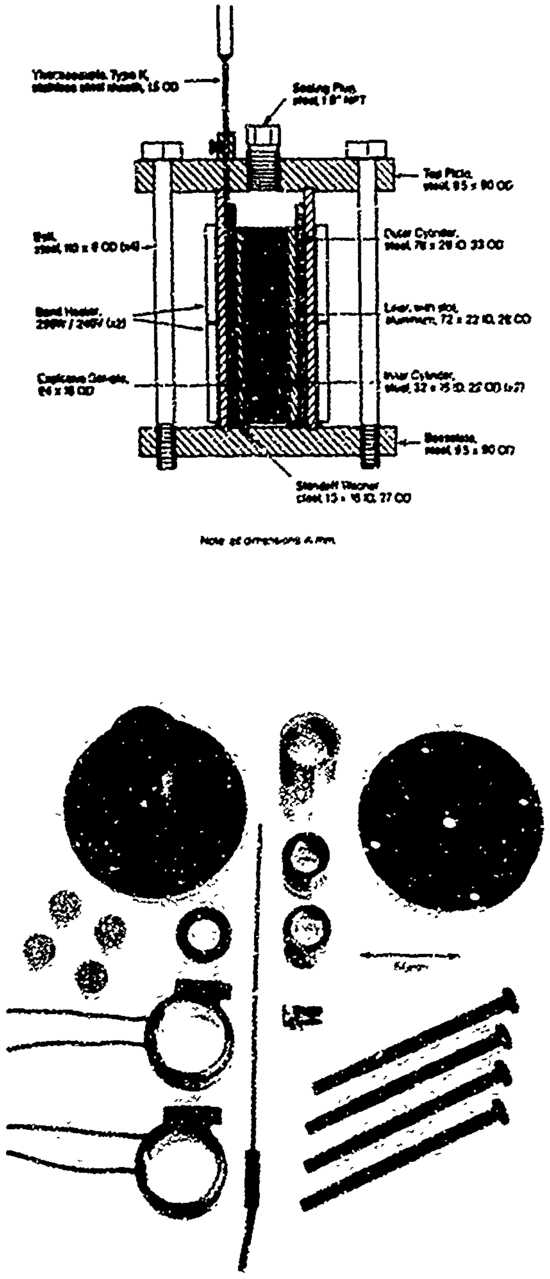
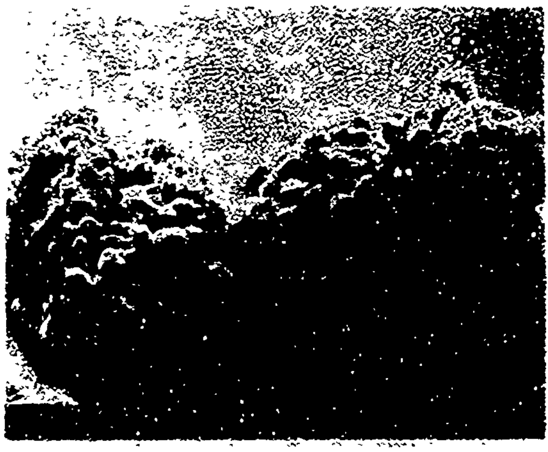


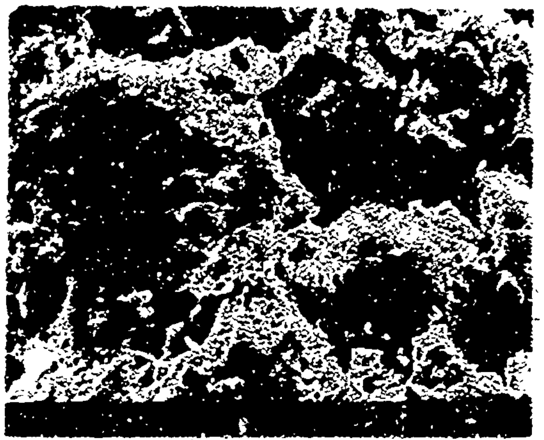
Figure 1 *The Super Small-scale Cookoff Bomb (SSCB). Diagrammatic (top), and prior to assembly (bottom).*

(a) RDX Grade A Class 1 (recrystallized)



(b) RDX/Levapren 452. A typical moulding granule of partly coated RDX crystals bound by polymer.

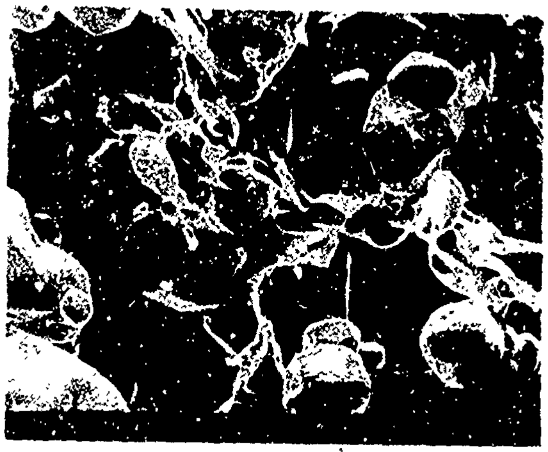
Figure 2 Scanning electron micrographs of (a) uncoated RDX, as used in RDX/EVA compositions, and (b) RDX/EVA (95:5) moulding granule.



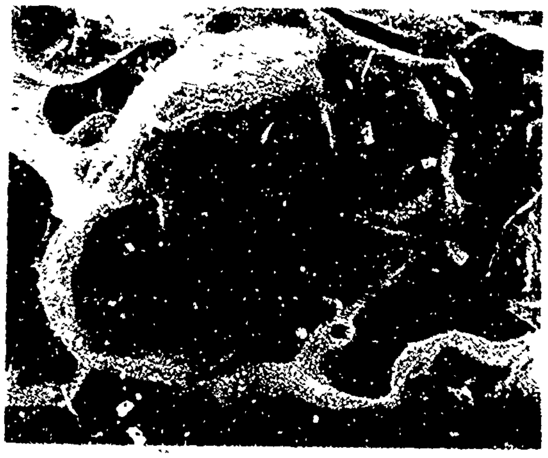
Micrograph A *RDX Vynathene EY 902-35. The polymer coating on the crystals is severely disrupted.*

Micrograph B *RDX/Elvax 650. Textured polymer on the leading face and the surround faces uncoated.*

Figure 8 *Scanning electron micrographs of RDX/EVA (95:5) compositions prepared by the general method.*

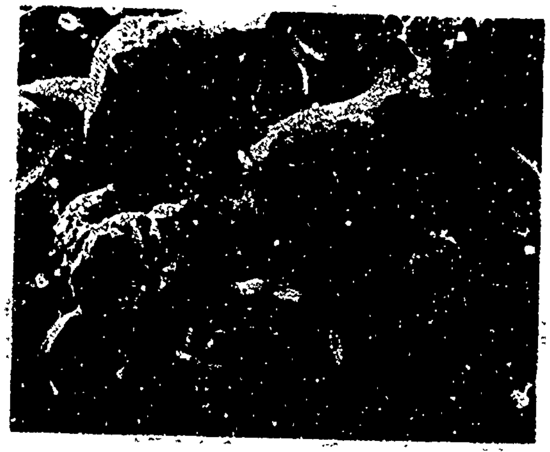


Micrograph C RDX/Elvax 650. Disruption of a granule reveals the polymer was largely deposited in polymer strands which bind the granule together.



Micrograph D RDX/Elvax 210. Large areas of uncoated crystals are clearly visible.

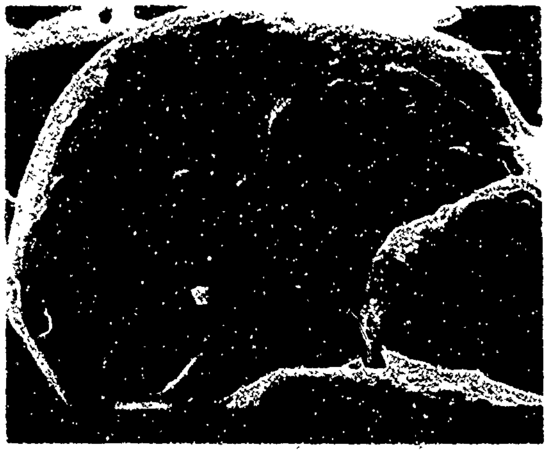
Figure 3 (continued) Scanning electron micrographs of RDX/EVA (95:5) compositions prepared by the general method.



Micrograph E RDX/Levapren 500. Crystals surfaces are well coated with a smooth polymer film.

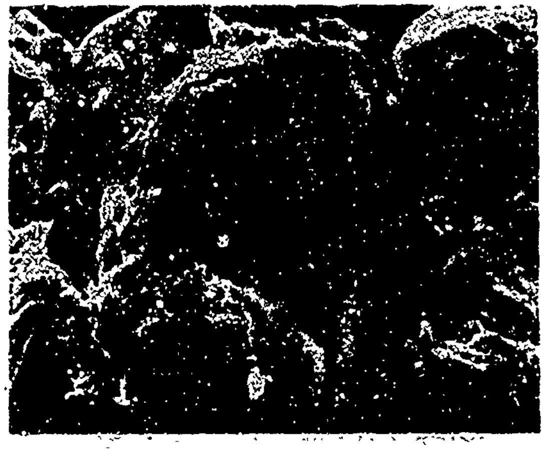
Micrograph F RDX/Levapren 452. Smooth well coated surfaces are obtained with lower molecular weight copolymers.

Figure 3 (continued) Scanning electron micrographs of RDX/EVA (95:5) compositions prepared by the general method.

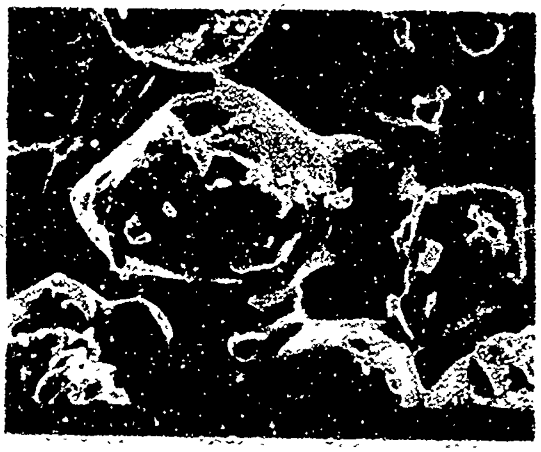


Micrograph G RDX/Levapren 450. Raised areas of polymer and areas of bare RDX crystal are indicative of poor flow of the polymer solution during coating.

Figure 3 (continued) Scanning electron micrographs of RDX/EVA (95:5) compositions prepared by the general method.



Micrograph A *RDX/Levapren 408. Disrupted polymer film on the exterior of granules prepared by the general method.*



Micrograph B *RDX/Levapren 408. Comparatively smooth exterior polymer coating obtained with a ratio of water to RDX of 5:1.*

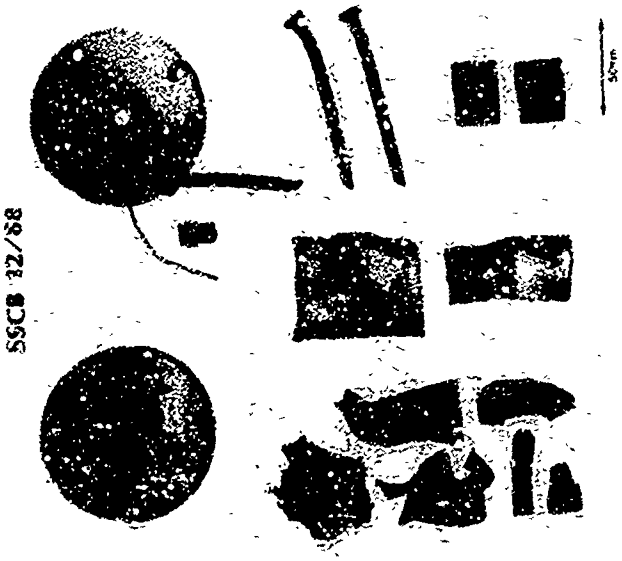
Figure 4 *Scanning electron micrographs of RDX/Levapren 408 (95:5) and RDX/Elvax 210 (95:5) compositions. The slurry coating conditions varied are indicated in each case.*

Micrograph C *RDX/Levapren 408. The anionic surfactant additive results in a smoother, improved but incomplete film of polymer coating on the RDX crystals.*

Micrograph D *RDX/Elvax 210. The anionic surfactant additive causes the polymer to be deposited in droplets leaving large areas of exposed RDX.*

Figure 4 *Scanning electron micrographs of RDX/Levapren 408 (95:5) and RDX/Elvax 210 (95:5) compositions. The slurry coating conditions varied are indicated in each case.*

(a) Detonation, from RDX/Viton A 95/5, fast heating rate.



(b) Deflagration, from RDX/Levapren 500 95/5, fast heating rate.

Figure 5 *Typical results of SSCB tests, showing (a) detonation, and (b) mild reaction.*

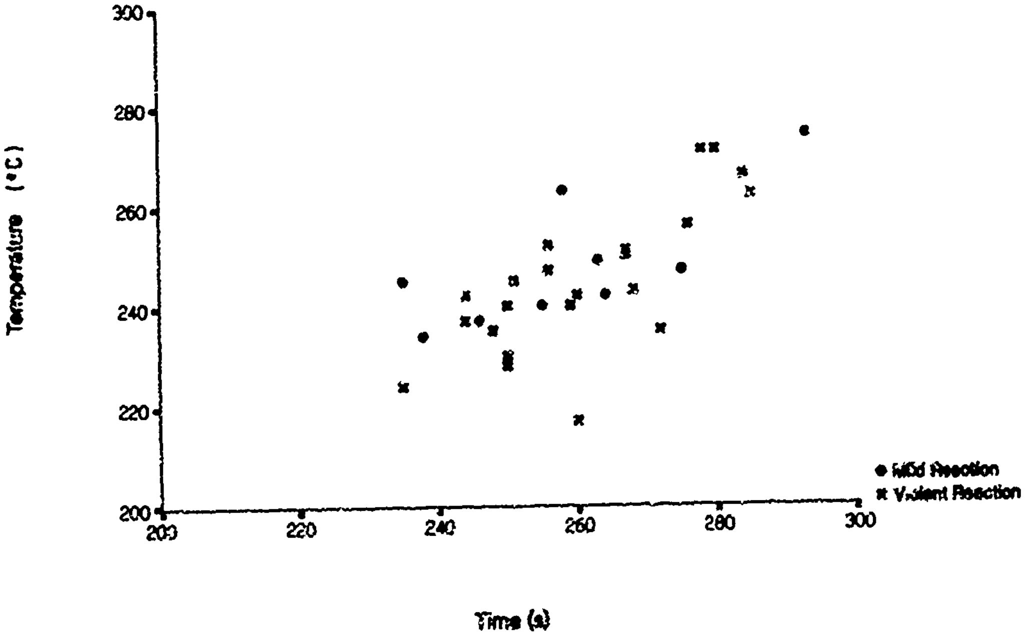


Figure 6 *RDX/EVA (95/5) Compositions. SSCB Tests at Fast Heating Rate Time - Temperature - Type of Response*

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An evaluation of ethylene-vinyl acetate copolymers as desensitizers for RDX in insensitive booster compositions prepared by slurry coating technique

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ABSTRACT

Twelve ethylene-vinyl acetate (EVA) copolymers with vinyl acetate contents ranging from 12 to 51% have been evaluated as desensitizers for RDX, for production of insensitive booster compositions. The RDX/EVA compositions were prepared by a solvent-slurry coating process, in which a solution of the EVA copolymer in a suitable solvent is added to an aqueous suspension of RDX, the solvent then being removed by distillation to effect coating of the polymer on the RDX. The efficiency with which the EVA copolymers coat the RDX crystal surfaces increases with increasing vinyl acetate content, and can be altered by the use of surfactants.

The RDX/EVA compositions all have excellent thermal stability, as assessed by the vacuum thermal stability test. The shock sensitivities of compositions prepared with copolymers containing 28 to 51% vinyl acetate were found to be between those of tetryl and PBXW-7, with the shock sensitivity generally decreasing with increasing vinyl acetate content. In general, the EVA coatings gave little desensitization to impact or cookoff; only one composition had a figure of insensitiveness (F of I) which meets current impact sensitiveness requirements for booster explosives for fuzes, and only two compositions gave mild reactions in small-scale cookoff tests. It is unlikely that an insensitive booster explosive composition containing only RDX with an EVA coating could be developed; however, further work on systems using EVA copolymers with additional materials should be undertaken to further examine desensitization mechanisms and identify formulations which may produce insensitive booster compositions.

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