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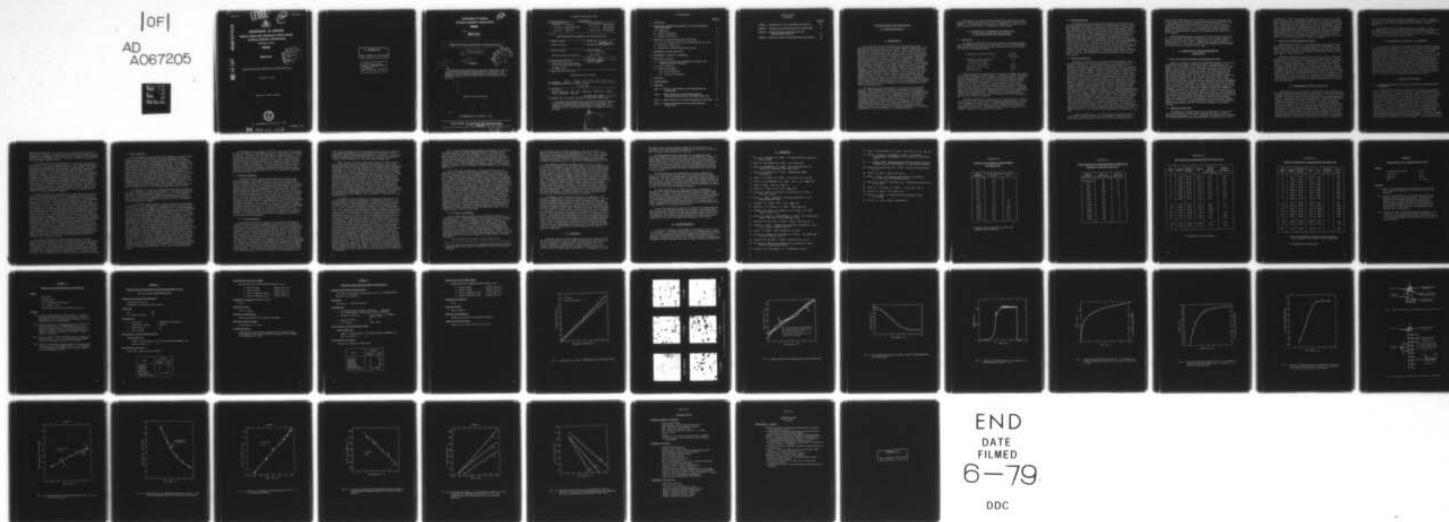
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RDX/POLYETHYLENE WAX COMPOSITIONS AS PRESSED EXPLOSIVES

William S. Wilson

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REPORT

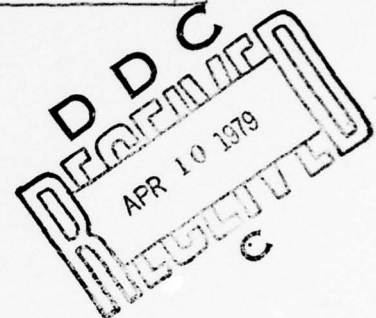
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(10) William S. Wilson

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ABSTRACT



The preparation and sensitivity of explosive formulations prepared from RDX and an emulsifiable polyethylene wax are described. The compaction of these explosive compositions, the sensitivity of the resultant charges to shock and their velocity of detonation are also discussed.

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The preparation and sensitivity of explosive formulations prepared from RDX and an emulsifiable polyethylene wax are described. The compaction of these explosive compositions, the sensitivity of the resultant charges to shock and their velocity of detonation are also discussed.

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RDX/POLYETHYLENE WAX COMPOSITIONS

AS PRESSED EXPLOSIVES

1. INTRODUCTION

The low melting point of TNT (80.9°C [1]) has enabled Australian munitions to be filled with melt-cast TNT-based explosive compositions, which may be poured simply from steam heated vessels. However although this low melting point is an advantage from the point of view of shell filling, it is apparent that the same property could cause problems in a munition intended for use at or excursion to elevated temperatures, such as in a weapon carried externally on supersonic aircraft. Further the low strength of TNT-based compositions makes such fillings susceptible to cracking when subjected to severe pressures during gun-firing and at target impact [2]. Such cracks can contribute to the premature functioning of the ammunition. Unadulterated high temperature explosives are often quite sensitive to a variety of stimuli, and are difficult to process as the coherent charges required for munition fillings. Two basic approaches are commonly adopted to obtain processable temperature and shock resistant formulations. The first involves the use of a polymer bonded explosive (PBX), a suspension of an explosive with a high melting point in a polymeric binder, which is poured or extruded into the round and allowed to cure *in situ* to obtain a solid charge. The second approach is to coat a powerful high melting explosive such as PETN or RDX with an inert material, commonly a wax, to act as both binder and desensitiser, and to compress the resultant composition to form a solid charge. The current project is intended to provide information about and understanding of this type of pressed explosive.

The compositions under consideration in this exercise contain RDX, powerful, readily available and relatively inexpensive, as the explosive component, and an emulsifiable polyethylene wax, which has been suggested as a possible phlegmatiser to replace or supplement beeswax in Composition B [3], as the binder-cum-desensitiser. This emulsifiable wax has also been used with HMX and terylene fibre to prepare EDC 23 and EDC 24, two powerful heat resistant explosives developed at AWRE, Aldermaston, U.K. (In the early development stages of the KARINGA system it was suggested that an RDX/polyethylene wax composition of the proportions 92:8 should be used as a bomblet filling. However the relatively high shock sensitivity of the explosive and hence the possibility of sympathetic detonation of the bomblets precluded the use of the explosive in this application [4]).

This report, then, describes RDX/polyethylene wax compositions, their preparation and explosive sensitivity, and their compaction to form explosive charges. It further discusses the effects of composition and density on the shock sensitivity and velocity of detonation of these charges.

2. PREPARATION, APPEARANCE AND SENSITIVITY OF RDX/POLYETHYLENE WAX COMPOSITIONS

2.1 Preparation

The explosive compositions used in this study were prepared from RDX Grade 1A (DEF(AUST)382; equivalent to RDX Grade A, Class 1 of DEF(AUST)5382) and an emulsifiable polyethylene wax AC629 manufactured by Allied Chemicals Ltd. with the following properties :

Melting Point (ASTM E28-5IT)(°F)	213-221
(°C)	100.6-105.0
Penetration (ASTM D 1321-55T) (100 g/5 s/77°F/dmm)	3-6
Acid Number (mg KOH/100 g)	14-17
Viscosity at 140°C (Pa.s)	0.140
Specific Gravity	0.93

RDX/polyethylene wax compositions were prepared with nominal wax content 1-15% using the AWRE wax emulsion process. The method is simple, but details are not readily available in the literature, and the procedure is therefore outlined in Appendices 1 and 2. Briefly, an emulsion of the wax in water, oleic acid and morpholine was added to a slurry of RDX in water, and the emulsion was broken by the addition of dilute sulphuric acid to the hot mixture (95°C). After washing with distilled water to remove all traces of acid the explosive powder was dried to constant weight at 70°C. (It appears that moist polyethylene is particularly susceptible to attack by fungus and mould, and it has therefore been suggested that the final wash should contain 0.05% methyl *p*-hydroxybenzoate. This precaution was also taken for the present study, although in every case the explosive was dried immediately, and no trace of mould was detected).

The RDX/polyethylene wax compositions were then submitted for analysis of wax content. The results of these analyses are given in Table 1, and are shown in graphical form in Figure 1. A more detailed analysis was carried out on explosive of nominal composition 92:8 to determine the presence of morpholine and oleic acid. Both compounds were found to be present, to the extent of 0.004% and 1.0% respectively by weight.

2.2 Physical Appearance

The RDX/polyethylene wax compositions prepared by this method may be described generally as cream coloured, free-flowing granular powders. However the powders vary somewhat in appearance with the amount of wax present. The compositions of low wax content are fine, almost white powders, while those with larger proportions of wax are made up of larger granules, and are more yellow in colour. Various RDX/polyethylene wax compositions and, for comparison, RDX Grade 1A were examined using a binocular stereomicroscope; photomicrographs taken through one eye-piece are reproduced in Figure 2. While the unwaxed RDX Grade 1A is present as individual small crystals, the particles in the composition RDX/polyethylene wax 99:1 are clearly aggregates of RDX crystals and wax. It may be inferred from the rough irregular surfaces of these particles that the wax does not actually coat the explosive, at least at these small concentrations, but rather the RDX crystals are embedded in the surface of discrete particles of wax. As the proportion of wax present in the composition increases the aggregates become larger, smoother and more rounded. This suggests that, as the wax content increases, the wax tends to fill the inter-crystalline crevices, and possibly even coats the RDX crystals.

2.3 Explosive Sensitivity

Compaction of explosives is an inherently hazardous operation, and it is clearly important to know the sensitivity of a new composition before pressing it into pellets. At Materials Research Laboratories this is commonly provided by an Explosives Safety Certificate, in which are compiled the results of tests designed to assess the sensitivity of the explosive to a variety of stimuli - impact, friction, frictional impact, ignition by heat, flash and electrical discharge - and its chemical stability. Rather than testing each composition for sensitivity to every stimulus, a median composition in the range was selected, namely RDX/polyethylene wax of nominal composition 92:8, and submitted for full Explosive Safety Certificate testing. The results are presented in Appendix 3, and may be compared with those in Appendix 4 obtained for the dry, unwaxed RDX Grade 1A from which the compositions were prepared. Only in three respects was the waxed explosive significantly different from the untreated RDX - ignition by electrical spark, chemical stability and sensitivity to direct impact. RDX Grade 1A can be ignited by an electrical spark with energy 4.5 J, whereas the RDX/polyethylene wax composition cannot. Somewhat more importantly, although RDX/polyethylene wax 92:8 is quite stable at 120°C it shows some chemical decomposition at 150°C, at which temperature RDX itself is stable. Thus the range of thermal stability of this formulation, while better than that of TNT-based compositions, is clearly limited. In addition, RDX/polyethylene wax 92:8 has a Figure of Insensitiveness (F of I) of 149 in the Rotter Impact Test, with a mean volume of gas evolved 4 ml, compared with RDX Grade 1A which has a F of I of 80 and a mean gas volume of 17 ml. The sensitivity of an explosive to ignition by an electrical spark is not particularly relevant to the compaction process, but the F of I is clearly important, and further analysis of the impact sensitivity of the RDX/polyethylene compositions was therefore carried out.

In order to measure the F of I of an explosive composition using the Rotter Impact Machine, a sample of a few milligrams of composition in a metal cap is placed between a striker and an anvil, and a 5 kg weight is

dropped from a known height on to the striker. The test is repeated with the drop height being decreased or increased depending on whether the result of the preceding test was an 'explosion' or not, the criterion for an 'explosion' being the evolution of not less than 1 ml of gas recorded by a special gas measuring burette. The 50% 'explosion' height is calculated using the Bruceton method [5], and is compared with the 50% 'explosion' height for a special grade of RDX used as a standard and to which a F of I of 80 is assigned.

Each RDX/polyethylene wax composition, with wax contents varying from 0 to 15%, was therefore tested for sensitivity to direct impact using the Rotter Impact Test. The results are given in Table 2, and are shown in graphical form in Figures 3 and 4. Compositions containing a nominal 4% wax or more had F's of I in excess of about 130, and provided normal precautions were taken they were considered safe to press.

3. COMPACTION OF RDX/POLYETHYLENE WAX COMPOSITIONS

3.1 Use of the 'Instron' Universal Testing Machine as a Press

In order to assess the variation of detonation parameters as a function of composition and density, the RDX/polyethylene wax compositions were pressed into 2.50 g pellets 0.50 in (12.7 mm) in diameter and about the same length. The pellets were pressed individually in a nest of five half inch diameter moulds, using as a press an 'Instron' Universal Testing Machine Model TT-CM operating in the compression mode with an FRM-type load cell. The 'Instron' machine is normally used for conventional compressive and tensile testing of materials. The test piece is fitted between a fixed stop and a moving crosshead, and a chart recorder monitors the load (either compressive or tensile) on the test-piece. Load cycling cams and switches on the chart recorder permit automatic cycling between two previously determined loads. By adjusting the maximum load cam to the desired load and the minimum load cam to a greater load value, the automatic load cycling facility may be used to maintain a constant load on the sample by incremental movement of the crosshead. In Figure 5 is reproduced a typical record for the compaction of RDX/polyethylene wax 92.5:7.5 for 2 minutes in a half inch mould (12.7 mm) at a load of 2.07 kN and a crosshead speed of 0.5 mm min⁻¹. The amplitude of the load oscillations depends on the differential load required to operate the switch (about 0.5% full scale deflection), the recorder and crosshead reaction times, the crosshead speed and the relaxation time of the test material (explosive composition). For all experiments the lowest possible crosshead speed, viz 0.5 mm min⁻¹, was employed during application of the pressing load, although higher speeds were used to move the crosshead to the required position.

3.2 Selection of Dwell Time

The density of a compact produced by the application of a given load will clearly depend on the dwell-time, the period of time for which the pressing load is applied. In order to determine the dwell-time most suitable for pressing RDX/polyethylene wax compositions, the variation with time of

the length of a pellet of explosive was monitored as the pellet was pressed under a constant load. RDX/polyethylene wax 92.5:7.5 (2.0 g) was pressed in a half inch mould with a dead load of 3.97 kN and a crosshead speed of 0.5 mm min⁻¹. The movement of the crosshead and, indirectly, the change in density of the pellet after the first application of the 3.97 kN load were monitored using a displacement gauge (Philips PR 9310/03) and a carrier wave measuring bridge (Philips PR 9304). The variation of explosive density with pressing time is illustrated in Figure 6, which indicates that the density is still increasing even after the load has been applied for 10 minutes. However since such a dwell-time is clearly impractical for pressing pellets in large numbers, an arbitrary compromise of 2 minutes was adopted.

3.3 Production of RDX/Polyethylene Wax Pellets

RDX/polyethylene wax 92.5:7.5 was pressed into 2.50 g pellets 0.50 in (12.7 mm) in diameter using the 'Instron' Universal Testing Machine in the manner described above, with a crosshead speed of 0.5 mm min⁻¹ and a dwell-time of 2 minutes, and with the pressing load being varied between 2.07 kN and 14.90 kN. The variation of the density of the pellets with the pressing load applied is shown in Figure 7.

RDX/polyethylene wax of compositions 96.15:3.85 to 86.5:13.5 were also pressed into 2.50 g pellets 0.50 in (12.7 mm) in diameter using a constant pressing load of 4.90 kN, with a crosshead speed of 0.5 mm min⁻¹ and a dwell-time of 2 minutes as previously. It was expected that this would produce compacts of constant voidage, and thus of density constant relative to the theoretical maximum density (TMD) for the particular composition. However, as Figure 8 reveals, this proved not to be the case and the compressibility of compositions containing less than about 9% of wax, indicated by the density attained by pressing at 4.90 kN, depends markedly on that wax content. On the other hand compositions containing 9.6% of wax or more were compressed to a constant density of $95.3 \pm 0.2\%$ TMD (4.7% voidage) by the application of the 4.90 kN load, and RDX/polyethylene wax compositions 95.2:4.8 and 93.25:6.75 were therefore pressed to this density, using pressing loads of 11.97 kN and 7.91 kN respectively.

4. MEASUREMENT OF SHOCK SENSITIVITY

The sensitivity of an explosive to initiation by shock is measured at Materials Research Laboratories using an adaptation of the Gap Test described by Cachia and Whitbread [6] and illustrated in Figure 9. Briefly, a standard detonator (the Scale 1 Gap Test Donor, comprising an exploding bridge wire to initiate a low density PETN charge which detonates a high density PETN pellet) generates a standard shock which is attenuated by a stack of laminated 0.002 inch brass shims 1 in (2.54 cm) square. The attenuated shock wave strikes the receptor or test explosive, usually a cylindrical pellet 0.50 in (12.7 mm) in diameter and 1.0 in (25.4 mm) long, which rests on a mild steel witness block. If on firing the assembly a deep, sharply defined dent is produced in the witness block, the test explosive is said to have detonated. The thickness of brass required to prevent 50% of detonations in the test explosive is determined by the Bruceton 'staircase' procedure [5] in which the gap thickness is increased or decreased by an increment of 0.004 inches (0.002 inches if the critical gap is less than 0.040 inches) depending on

whether the previous firing produced a detonation or a failure. Normally 25 'shots' are fired after the approximate median point has been established, although fewer can be used if quantities of test explosive available so dictate.

This method was used to determine the shock sensitivity of RDX/polyethylene wax 92.5:7.5 at various densities, and of RDX/polyethylene wax of varying compositions pressed to a density of 95.3% TMD. Two pellets 0.50 in (12.7 mm) long stacked end-on-end were used for each receptor charge. The results of these tests are found in Table 3.

5. MEASUREMENT OF VELOCITY OF DETONATION

The velocity of detonation of an explosive charge is commonly measured at Materials Research Laboratories by means of high speed streak photography or ionization probe techniques. For the current study the latter method was employed, using the experimental assembly in Figure 10. Ten pellets of pressed RDX/polyethylene wax 0.50 in (12.7 mm) in diameter and about the same length were measured accurately and stacked end-on-end with two brass strips 2 mm wide and 0.05 mm thick placed about 2 mm apart between each pair of pellets to act as ionization probes. A voltage source was applied between the brass probes, the assembly was initiated by an exploding bridgewire detonator, and the electrical pulses produced as the detonation front passed each ionization probe were recorded using a time-calibrated oscilloscope. The velocity of detonation was calculated from the inter-probe distances and the time between pulses. This method was used to measure the velocity of detonation of RDX/polyethylene wax 92.5:7.5 at varying density, and of RDX/polyethylene wax of varying compositions pressed to a density of 95.3% TMD. The results of these experiments are presented in Table 4.

6. DISCUSSION OF RESULTS

6.1 Initiation, Deflagration-to-Detonation Transition and Desensitisation of Explosives

It is now accepted that the initiation of an explosive is a thermal process, regardless of the source and nature of the exciting stimulus [7]. Usually, however, this stimulus provides less energy than would be required to initiate uniform reaction of the explosive sample as a whole, and it has been necessary to postulate the concentration of this energy at suitable 'hot spots' where reaction is initiated and from which, if conditions are favourable, the reaction can grow in strength until a stable detonation results [8]. Numerous mechanisms have been proposed to account for the generation of hot spots in heterogeneous explosives. These include inter-crystalline friction under compression [9], adiabatic compression [10] and propulsion of explosive dust particles through hot, interstitial gases and into the opposite walls of cavities [11,12], and local convergence and reinforcement of small shocks at inhomogeneities in the explosive [13]. Each of these mechanisms could contribute to the generation of hot spots, depending on both the explosive and the initiating stimulus. In each case the mechanism operates at inhomogeneities in the explosive - voids, grain boundaries,

internal crystal defects, etc. - and it is at these sites that the onset of reaction may be detected. Indeed there is also evidence to suggest that the initiation of a homogeneous explosive involves the disruption of the material and generation of potential hot spot sites first, followed by initiation of reaction in these regions [11,14].

If the reaction at a hot spot develops so that energy is released at a sufficient rate for a self-sustaining process to occur, deflagration results. The explosive is consumed not homogeneously but 'cigar-fashion' in Eyring's grain-burning mechanism [9], with the energy released being transmitted to the unburnt explosive by the relatively slow conductive and convective transport processes. The linear deflagration rate is a monotonic increasing function of pressure, and it is this property which enables the burning of a condensed or confined explosive to develop to detonation. It is currently accepted that a rapid (exponential) increase in the build-up of pressure from the combustion products as a consequence of their confinement results in a series of strong compressive waves which coalesce to form a reactive 'precursor shock'. When this shock is sufficiently strong it develops to a stable detonation wave [15]. It is apparent that important factors relevant to the rapid pressure build-up required include the rate of reaction, the volume and energy of gaseous reaction products, their confinement and the transfer of energy to unreacted explosive.

Military explosives are frequently much more sensitive than is acceptable for use in a particular role, and as a consequence waxes and similar inert materials have been added to act as 'phlegmatisers', reducing sensitivity to such stimuli as shock, impact and friction [16]. Such desensitisation could be the result of preventing either initiation or growth and propagation of reaction. Initiation might be prevented by direct absorption by the additive of the energy imparted by the external stimulus, inhibiting the generation of hot spots. On the other hand the additive might also act as a thermal sink to absorb energy from those hot spots generated, isolating and quenching them and thereby preventing growth and propagation through the bulk of the explosive. It was suggested by Linder [17] that the number of hot spots generated is not greatly reduced by the presence of wax, but that reaction does not propagate so freely from them. It is clear that, although the melting point and hardness of the desensitiser are undoubtedly significant, the properties of *major* importance are the specific heat, which governs the amount of energy which can be absorbed, and the distribution of the wax throughout the explosive [18]. The desensitisation will be most effective if the wax is apportioned to all potential hot spot sites, eliminating them entirely or absorbing the energy produced and insulating them from the bulk of the explosive. It follows that, if the wax is efficiently dispersed, a critical concentration of wax should be reached when all cavities and interstices are filled and all explosive crystals have received an appropriate surface coating, above which no further desensitisation can occur, and further wax acts simply as a diluent.

The waxes incorporated into pressed explosives serve a two-fold purpose: to render the explosive composition less sensitive to stray energy pulses as described above, and to act as a binder and lubricant during the compaction process. The effectiveness of the polyethylene wax as a binder-cum-lubricant in the RDX/polyethylene wax system is illustrated in Figure 8, which shows the densities achieved by compressing various compositions under a constant load. Compositions containing more than ca. 10% wax are clearly much more readily compressed than are those which contain smaller proportions.

6.2 Impact Sensitivity

The fundamental processes which occur during impact testing are quite complex, and are not well understood at least in quantitative detail. Important parameters must include the pressure-time profile of the pulse experienced by the explosive, determined *inter alia* by the geometry of the anvil and striker, their elastic properties and those of the explosive, and the confinement and flow of explosive during the test. Other relevant properties include coefficients of friction, hardness and heat capacity [7]. In more general terms, it has been shown that initiation by impact occurs at hot spots created by deformation and friction of the explosive, gas compression and mutual reinforcement of small shock waves [8]. It is stated that, in the Rotter Impact Test, the Figure of Insensitiveness (F of I) gives a measure of the energy required for the initiation of the explosive by impact, and that the mean volume of gas evolved reflects the ease of propagation of the reaction [19]. While this is a useful approach, it must be appreciated that this picture is not quite unequivocal, since the criterion used to define the occurrence of initiation is that the reaction grows or propagates until 1 ml of gaseous products have been released.

The dependence of the F of I of RDX/polyethylene wax on the composition of the explosive is illustrated in Figure 3. This graph indicates that the impact sensitivity decreases steadily from an F of I of 80 typical of pure RDX to a value of 204 for a composition containing 15% by weight of wax. (An F of I of 200 is considered to be about the upper limit of the Rotter Impact Machine, and a material with such an F of I is considered to be quite insensitive to impact).

Two curves which might possibly be used to describe the relationship between F of I and the composition of the explosive are included in Figure 3. The first, curve (a), might be rationalised in terms of the desensitisation of the explosive by elimination and insulation or isolation of potential hot spot sites. Thus voids and cavities are progressively filled and the explosive crystals are coated by a critical thickness of wax - i.e. the wax is both absorbed and adsorbed by the explosive - and the impact sensitivity is reduced in the apparently 'two-stage' sequence. However the F of I of an explosive can vary slightly from one test to another depending on such parameters as anvil condition, atmospheric humidity and 'operator variables', and experimental results are normally rounded to the nearest multiple of ten [20]. Further, there is evidence that polyethylene wax does not actually coat the RDX, at least for compositions of low wax content, but rather the wax is present in discrete globules into whose surfaces the explosive crystals are embedded [21]. (It is noted, however, that the agglomerates of RDX/polyethylene wax composition illustrated in Figure 2 become larger in size and more regular in form with an increase in wax content, and it may safely be inferred that the surface of explosive covered by wax also increases at the same time). This being so, it is probably unwise to ascribe a specific curve such as (a) to the relationship between impact sensitivity and wax content. It would be more prudent simply to conclude that F of I increases steadily with wax content, and to avoid discussing the relationship in terms of the mechanisms of desensitisation. Indeed it is noted that the linear plot (b) can be drawn to pass within 10 F of I units of all experimental points.

The dependence on wax content of the mean volume of gas evolved during Rotter Impact Testing of the RDX/polyethylene wax compositions is illustrated in Figure 4. This graph shows that the mean gas volume decreases from 18 ml for pure unwaxed RDX to 1 ml, the lower limit for the test procedure, for compositions containing more than about 10% wax. Thus it may be concluded that the presence of polyethylene wax in the composition retards the propagation of explosive reaction, in addition to rendering initiation of the reaction by impact more difficult. In this regard these results support the conclusions of Copp and Ubbelohde [22] rather than those of Linder, who found that the presence of moderate quantities of wax inhibited the propagation of reaction in PETN and HMX, but had little influence on initiation by friction or impact [17].

6.3 Detonation Parameters

A shock wave passing through an inert medium loses energy as heat during compression of the material, and the velocity of the disturbance decreases steadily towards zero. However if the compressed medium can be made to decompose and give up energy sufficiently rapidly under the influence of the shock wave, there will be a stable equilibrium condition at which the chemical energy released and transmitted to the reaction front matches the energy dissipated during compression of the unreacted material, and the shock velocity will stabilise at a constant value. A shock wave transmitted into an explosive charge may be faster than, the same velocity as, or slower than the stable detonation wave for that composition. An overdriven shock wave, faster than the stable wave, always decays until the equilibrium condition is reached and maintained by transmission of energy from the reacting explosive to the shock front. An underdriven shock wave can either build up to stable detonation or decay to zero. In such a case the thermal energy developed by the passage of the shock wave through an explosive is available to initiate reaction at hot spots. If this reaction can develop sufficiently rapidly detonation will ensue; if the reaction is quenched or does not accelerate sufficiently rapidly the shock wave will simply decay. Thus the behaviour of an explosive under the influence of a shock wave is dependent not only on initiation of reaction but also on propagation and growth of this reaction to full detonation.

6.3.1 Shock Sensitivity

The shock sensitivity of an explosive is a measure of the smallest underdriven shock wave which can develop to detonation in that explosive. A number of conditions must be satisfied before the critical shock required for initiation of the explosive can be determined. First the incident shock wave must be a suitably stable plane wave of known amplitude and duration. Second the receptor charge, the explosive under test, must be sufficiently large in diameter to avoid complications from edge effects, and it must be long enough for the reaction to achieve stable detonation. In practice the first two conditions are seldom met in the Gap Test - the incident wave is not planar and the shock wave in the receptor is subject to side rarefactions and reflections - and growth to full detonation is determined by an impression in a witness plate rather than by monitoring the attainment and maintenance of a constant shock velocity. Further, the result of the test is normally expressed as the critical barrier thickness which will allow 50% initiation of the explosive. The system may be calibrated to give the strength of the shock passing through a given barrier thickness, but determination of the

actual shock transmitted into the test explosive also requires a knowledge of the impedance mismatch at the barrier-explosive interface, which is dependent on both the composition and density of the explosive. Nonetheless valuable information may be obtained using this technique to measure the critical barrier thickness for a series of similar compositions.

There is little consistent information available regarding variation of the shock sensitivity of an explosive with its density. Many workers suggest that shock sensitivity decreases with increasing density, as reported for example by Savitt, Leone and Kyselka for the "direct contact detonation sensitivity of, *inter alia*, TNT, TNB and tetryl at densities in the range 70-95% TMD" [23]. However results quoted from the Wax Gap Test for booster sensitivity of various pressed granular explosives are more equivocal. While single explosives such as TNT and tetryl show decreasing sensitivity with increasing densities, mixed explosives such as pentolite, Composition A-3 and PTX 1 and 2 show different trends. On the other hand the same publication quotes results from the Lucite or Small Scale Gap Test which indicate that the shock sensitivities of RDX, tetryl and TNT first increase with density to a maximum in the range 70-90% TMD, and then decrease again as density increases still further [24]. Indeed, it has been suggested that this is the usual effect of density on the shock sensitivity of an explosive. Yet a third set of experiments investigating the initiation of pressed tetryl by small charges of PETN suggests that, in the density range 1.45-1.65 (83-96% TMD), the denser compacts are more sensitive to initiation than the less dense [25].

The variation of shock sensitivity of RDX/polyethylene wax 92.5:7.5 with the density to which it is pressed is illustrated in Figure 11. The shock sensitivity of this explosive shows a steady increase as the density increases, with the critical thickness of brass barrier increasing from 42×10^{-3} in (1.06 mm) for explosive of density 1.50 Mg m^{-3} (89% voidless) to 70×10^{-3} in (1.78 mm) for explosive of density 1.62 Mg m^{-3} (96% voidless). This variation of shock sensitivity might be explained satisfactorily in terms of ease of initiation of reaction or transition from deflagration to detonation. In the first case it has been proposed [26] that there is a maximum size particle or void in a matrix of explosive which can react to a shock wave to generate hot spots, that size corresponding roughly to the "thickness" of the shock zone (the product of the duration and velocity of the disturbance). While smaller voids or bubbles tend to be carried along by the shock wave and so have more time to interact with it, larger discontinuities are simply skirted and bypassed. Thus, if increasing density is associated with a decrease in the size of interstitial voids without significantly reducing their number, frequency of initiation should increase as more and more of these defects become smaller than the critical size. Alternatively, the porosity and permeability affect grain burning and the transition from deflagration to detonation in an explosive [15]. Thus, if the hot gases produced during combustion are able to escape without giving up their energy to the unburnt explosive, the deflagration to detonation transition will be slower, and a more vigorous stimulus will be required to achieve detonation. If on the other hand the density is increased and the permeability of the explosive is reduced, the gas flow will become "choked" and the combustion products will remain in contact with the unburnt explosive longer, yielding up more of their energy. The transition from deflagration to detonation will be more rapid, and a more gentle stimulus will be required for detonation.

Each of these mechanisms seems reasonable in attempting to account for the results observed for pressed RDX/polyethylene wax. However three different tests have given three different results for the variation of shock sensitivity of tetryl with the density of the explosive, and some caution should be used in interpretation of results from the current tests. It would not be unreasonable to expect a similar dependence on the test configuration in the case of RDX/polyethylene wax. This dependence is presumably a function of such parameters as impedance mismatch at the barrier/explosive interfaces, and the critical and ideal diameters of the explosives under test.

On the other hand the dependence of the shock sensitivity of an explosive on its surface coating is better documented. It has been shown that the shock sensitivity of pressed HMX/wax 95:5 decreases markedly as the coating efficiency increases, regardless of the density of the compact [27]. Further, low density charges (ca 50% voidless) prepared from compositions of HMX and beeswax incorporated using an aqueous slurry technique show a decrease in shock sensitivity as the beeswax content is increased from 0 (critical barrier thickness 199×10^{-3} in (5.05 mm)*) to 10% (critical barrier thickness 20×10^{-3} in (0.51 mm)*) [28]. The variation with composition of the shock sensitivity of RDX/polyethylene wax pressed to a comparatively high density (95.3% voidless) is shown in Figure 12. Once again the shock sensitivity of the explosive is shown to decrease markedly with wax content. Given that an increase in wax content affords a more effective coating of the explosive crystals, these results may be satisfactorily explained in terms of deactivation of potential hot spot sites required for initiation, and/or inhibition of propagation of combustion in the explosive by the presence of the wax. However there is no evidence for a definite critical concentration of wax at which essentially all potential hot spot sites are eliminated and above which little further reduction in shock sensitivity might be anticipated. Perhaps this might be regarded as evidence for the propagation of microcracks ahead of the initiating shock wave, which can thereby generate its own hot spot sites.

6.3.2 Velocity of Detonation

From the data listed in Table 4 we can consider the velocity of detonation (V of D) of RDX/polyethylene wax as a function either of density or of composition. To this end Figure 13 shows the variation of V of D of RDX/polyethylene wax 92.5:7.5 with density or voidage, while Figure 14 indicates the variation of that parameter with the composition of RDX/polyethylene wax compressed to 95.3% of the theoretical maximum density (4.7% voidage). In each case linear regression on the experimental data resulted in the excellent straight line approximations illustrated, with correlation coefficients of 0.997 and 0.978 respectively. Indeed if all the experimental data are used and a least squares approximation is carried out with three variables (V of D, wax content and voidage content) the simple relationship

$$V \text{ of } D = 8979.0 - 55.4 (\% \text{ wax}) - 93.2 (\% \text{ voids}) \quad (\text{m/s})$$

* Note that these results should not be compared quantitatively with those from the present study because of differences in details of experimental procedure.

may be obtained with a multiple correlation coefficient of 0.988. As a measure of the accuracy of this approximation, the values of V of D calculated using this equation are presented in Table 4. In the worst case the difference between experimental and calculated values was 55 m/s, which corresponds to an error of 0.67%. This may be compared favourably with an estimated experimental error of at least 0.5% in the measurement of V of D.

The influence of density and composition on the V of D of RDX/polyethylene wax charges may be explained readily, if perhaps simplistically, in terms of the pressure of gaseous products generated in the reaction zone and the effects of that pressure on the shock front. The pressure produced depends *inter alia* upon the number of molecules and molecular weight of combustion products and on the chemical energy released in the reaction zone. If the density of an RDX/wax charge of fixed composition increases, the RDX contained in unit length (or volume) increases, with a resultant increase in both the number of molecules produced and the energy released in the reaction zone. The resultant pressure increase allows a more rapid and efficient transfer of energy to the shock front, thereby allowing the maintenance of a higher velocity shock wave. Similarly, if the relative density is held constant while the composition is varied, the number of molecules produced and the energy released will decrease as the wax content increases and the RDX content decreases. The pressure generated in the reaction zone will decrease, providing less efficient transfer of energy to the shock front, and the stable detonation wave resulting will be slower.

Two computer codes are available at MRL for the prediction of the pressure, temperature and velocity of detonation of an explosive. These are based on the Kamlet theory [29,30] and Mader's technique utilising the Becker-Kistiakowski-Wilson equation of state [31], which has been modified to run on the PDP-10 computer [32]. Both methods were used to predict the detonation parameters of RDX/polyethylene wax with various compositions and densities, assuming the wax to have a formula of CH_2 and a heat of formation of -20 kJ mol^{-1} ($-4.8 \text{ kcal mol}^{-1}$). The variation of the V of D predicted by each method with density and composition are shown in Figures 15 and 16, which also show the graphs of experimental results for the purpose of comparison. Surprisingly, since both codes are at least semi-empirical and are based on and fitted to well-established data obtained for common explosives such as TNT, PETN and RDX, the discrepancies between experimental and predicted results are quite large, particularly at high density and high wax content. Not so surprisingly the results from the more sophisticated BKW calculations fit the experimental data better than do those from the Kamlet code, but clearly neither system is really adequate for this class of explosive compositions.

7. CONCLUSION

Explosive powders of various compositions have been prepared from RDX and polyethylene wax by adding an aqueous morpholine/oleic acid emulsion of the wax to the RDX in an aqueous slurry, and breaking the emulsion at elevated temperatures by the addition of dilute sulphuric acid. The resultant explosive compositions are composed of discrete particles of wax in whose surfaces the RDX crystals are embedded. The aggregates of wax and

RDX become larger, smoother and more regular as the proportion of wax increases, and it might reasonably be inferred that the extent to which the RDX is coated by wax increases at the same time.

The RDX/polyethylene wax compositions can be regarded as being insensitive explosives. However the Figure of Insensitiveness given by the Rotter Impact Test varied from 80 for pure, unwaxed RDX to 204 for RDX/polyethylene wax 85:15, while the mean volume of gas evolved dropped from 18 ml for RDX itself to 1 ml, the limit of the test apparatus, for compositions with more than about 10% wax. It may be concluded that not only is the number of hot spots produced on impact testing reduced by the presence of wax, but the propagation of reaction in the explosive from these sites is also inhibited.

The RDX/polyethylene wax compositions were readily compacted as 0.50 in (12.7 mm) diameter pellets, using the Instron Universal Testing Machine as a press, for the measurement of shock sensitivity and velocity of detonation. The 'ease of pressing' of the compositions depended markedly on the wax content. Below about 9% wax the density of the compact (relative to the theoretical maximum or voidless density) achieved by pressing at a load of 4.90 kN increased with wax content, but above this wax content the density attained under this load was essentially constant.

The shock sensitivity of the RDX/polyethylene wax compositions increases with increasing density (decreasing voidage) and decreases with increasing wax content. These results can be explained in terms of either the hot spot initiation of reaction by the shock wave at cavities, voids and intercrystalline boundaries, or the influence of porosity and permeability on the propagation and development of this reaction to detonation. In either case the important features would appear to be cavities, voids and other inhomogeneities within the explosive charge, their interconnection and their elimination by the presence of the wax.

It was also shown that the velocity of detonation of RDX/polyethylene wax decreases with increasing voidage or wax content. These effects have been rationalised in terms of the pressure of gaseous products generated in the shock zone and the effects of that pressure on the shock front. It was noted however that neither the Kamlet approach nor the BKW code predicts adequately the velocity of detonation for explosives of this class.

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T A B L E 1

ANALYSIS OF WAX CONTENT IN RDX/POLYETHYLENE
WAX COMPOSITIONS

Nominal Composition	Acetone Insoluble Wax (%)	Total Wax* (%)
99:1	0.9	
98:2	1.6	
97:3	2.5	
96:4	3.4	
95:5	4.2	
94:6	5.2	
93:7	6.1	
92:8	6.7	7.5
91:9	7.8	8.7
90:10	8.6	9.6
89:11	9.6	10.8
88:12	10.4	11.6
87:13	11.2	12.5
86:14	12.1	13.6
85:15	13.0	14.6

* Includes acetone soluble wax and oleic acid
remaining from the emulsion.

T A B L E 2

IMPACT SENSITIVITY OF RDX/POLYETHYLENE WAX COMPOSITIONS
DETERMINED BY THE ROTTER IMPACT TEST

Nominal Composition	Figure of Insensitiveness	Mean Gas Volume (ml)
RDX Grade 1A	81	18
99:1	105	17
98:2	110	17
96:4	130	13
95:5	138	10
94:6	143	10
93:7	144	8
92:8	149	4
91:9	152	3
90:10	159	2
89:11	173	1
88:12	184	1
87:13	192	1
86:14	198	1
85:15	204	1

T A B L E 3

SHOCK SENSITIVITY OF RDX/POLYETHYLENE WAX COMPOSITIONS

Wax Content (%)	Density (Mg/m ³)	Relative Density (% TMD)	Voidage (%)	Critical Barrier Thickness (10 ⁻³ inches)	Standard Deviation (10 ⁻³ inches)
7.7	1.503	89.04	10.96	43.3	0.83
7.7	1.540	91.23	8.77	47.3	1.92
7.7	1.563	92.60	7.40	60.3	0.56
7.7	1.582	93.72	6.28	66.3	0.87
7.7	1.598	94.67	5.33	64.9	1.17
7.7	1.606	95.14	4.86	62.7	2.06
7.7	1.611	95.41	4.59	66.0	2.10
7.7	1.616	95.74	4.26	72.3	0.87
7.7	1.620	95.97	4.03	69.7	0.56
4.8	1.642	95.00	5.00	99.0	0.77
6.75	1.614	95.00	5.00	78.0	1.02
(7.7	1.607	95.21	4.79	68.0*)	
9.6	1.578	95.29	4.71	55.0	0.78
11.6	1.552	95.45	4.55	45.0	0.55
13.5	1.521	95.30	4.70	38.2	0.57
3.85	1.552	89.04	10.96	76.3	0.56
5.8	1.561	91.07	8.93	67.8	0.54

* Interpolated from results above.

T A B L E 4

VELOCITY OF DETONATION OF RDX/POLYETHYLENE WAX COMPOSITIONS

Wax Content (%)	Density (Mg/m ³)	Relative Density (% TMD)	Voidage (%)	V of D (m/s)	Standard Deviation (m/s)	Calc V of D* (m/s)
7.7	1.503	89.04	10.96	7544	5	7531
7.7	1.540	91.23	8.77	7754	5	7735
7.7	1.563	92.60	7.40	7908	4	7863
7.7	1.583	93.72	6.28	7988	4	7967
7.7	1.598	94.67	5.33	8061	4	8056
7.7	1.606	95.14	4.86	8113	4	8100
7.7	1.611	95.41	4.59	8126	4	8125
7.7	1.616	95.74	4.26	8194	3	8156
7.7	1.620	95.97	4.03	8221	4	8177
4.8	1.642	95.00	5.00	8192	5	8247
6.75	1.614	95.00	5.00	8111	8	8139
(7.7	1.607	95.21	4.79	8114**	-	8106)
9.6	1.578	95.29	4.71	7979	3	8008
11.6	1.552	95.45	4.55	7928	4	7913
13.5	1.521	95.30	4.70	7755	8	7793
3.85	1.552	89.04	10.96	7740	6	7744
5.8	1.561	91.07	8.97	7779	3	7822
12.5	1.510	93.61	6.39	7677	7	7691

* Velocity of detonation calculated from the equation

$$V \text{ of D} = 8979.0 - 55.4 (\% \text{ wax}) - 93.2 (\% \text{ voids}) \text{ (m/s)}$$

** Interpolated from results above.

APPENDIX 1

PREPARATION OF '25%' POLYETHYLENE WAX EMULSION

Reagents

Polyethylene Wax AC629	250 g
Oleic Acid	42 ml
Morpholine	37.5 ml
Water	to 1 litre

Procedure

- (i) Melt the polyethylene wax, and stir the oleic acid into the melt. Raise the temperature to 120-130°C and stir in the morpholine.
- (ii) Heat 650 ml distilled water to the boiling point and stir rapidly, taking care to avoid aeration. Add the melt (at 115-120°C) to the rapidly stirred water just below its boiling point. The stirring should be rapid enough to prevent solidification of the melt on the surface of the water during the addition process, which would result in the formation of large particles of non-emulsified polyethylene wax in the emulsion.
- (iii) Decrease the rate of stirring and allow the emulsion to cool to 40-50°C. Stop the stirring and leave the emulsion to stand, allowing entrained air to escape. Dilute the emulsion to 1 litre by the addition of distilled water, and store in a sealed container.

APPENDIX 2

PREPARATION OF RDX/POLYETHYLENE WAX COMPOSITIONS

Reagents

RDX Grade 1A
Distilled Water
'25%' Polyethylene Wax Emulsion
1-2 N Sulphuric Acid
0.05% Aqueous Methyl p-Hydroxybenzoate Solution

Procedure

- (i) Add the required amount of RDX (Grade 1A) to sufficient distilled water to prepare a 40% w/w slurry. Add the appropriate volume of polyethylene wax emulsion, and stir the mixture to an even consistency.
- (ii) Heat the mixture in a steam jacketted vessel to 85°C, and break the emulsion by the dropwise addition of 1-2 N sulphuric acid until the pH of the slurry reaches 4-5. During the addition of acid the slurry must be stirred as rapidly as possible to prevent the formation of large lumps of composition.
- (iii) Cool the slurry to 40°C by passing cold water through the jacketted vessel. Filter the solid and wash thoroughly with cold, distilled water until free from acid.
- (iv) Wash with 0.05% methyl p-hydroxybenzoate to prevent growth of mould on the stored explosive powder. Dry thoroughly at the filter pump, and finally dry to constant weight at 70°C and atmospheric pressure.

APPENDIX 3

EXPLOSIVES SAFETY CERTIFICATE DATA FOR RDX/POLYETHYLENE WAX 92:8

E&A : S.C.T. NO. 11 DATED 11 MAY 1972

Designation and General Characteristics

Polyethylene Coated RDX

COMPARATIVELY INSENSITIVE HIGH EXPLOSIVE

Composition

RDX 92%

A.C. 629 Polyethylene 8%

Classification

- | | |
|--------------------------|-----------------------------|
| a. Sensitivity | - Comparatively Insensitive |
| b. Storage and Transport | - Group 4 |
| c. Safety Distance | - ZZ |
| d. Fire Fighting | - 2 |

Sensitiveness to Direct Mechanical Shock

Rotter Impact Test

Figure of Insensitiveness - 140 (against RDX MRL STANDARD = 80)

Mean Gas Volume, ml - 1.3

Sensitiveness to Friction

Mallet Test (Expressed as percentage)

Anvil	Mallet	
	Boxwood	Steel
Yorkstone	0	50
Hardwood	0	0
Softwood	0	0
Mild Steel	)	
Naval Brass	)	Not Tested
Aluminium Bronze	)	

Sensitiveness to Practical Impact

Glancing Blow Test (Minimum Ignition Energy), joule.

- | | |
|-----------------------------|-------------------|
| a. Steel on Steel | Greater than 11.0 |
| b. Brass on Steel | Greater than 11.0 |
| c. Steel on Bakelised Cloth | Greater than 11.0 |
| d. Brass on Bakelised Cloth | Greater than 11.0 |

Temperature of Ignition (Degrees Celsius)

210°C

Ignition by Flash

Fails to ignite.

Behaviour on Inflammation

Ignites and supports train steadily throughout.

Ignition by Electric Spark

No ignitions at 4.5 joule.

Chemical Stability

Stable under vacuum stability conditions for 40 hours at 120°C;
but decomposes under vacuum stability conditions at 150°C (Normal
Test Temperature for RDX).

APPENDIX 4

EXPLOSIVES SAFETY CERTIFICATE DATE FOR RDX GRADE 1A

Designation and General Characteristics

RDX Grade 1A (equivalent to RDX Grade A, Class 1, of DEF(AUST)5382)

SENSITIVE HIGH EXPLOSIVE

Composition

RDX Grade 1A - Boiling Batch 1515

Classification

- a. (i) Sensitiveness to Impact & Friction : Sensitive
(ii) Sensitiveness to Electrostatic Sparks : Sensitive
- b. Storage and Transport - Group 10 (Dry - 1 oz sample)
Group 3 (Wet)
- c. Quantity Distance - ZZ
- d. Fire Fighting - Class 3 (Wet)

Sensitiveness to Direct Mechanical Shock

Rotter Impact Test

Figure of Insensitiveness - 80 (against RDX MRL STANDARD = 80)

Mean Gas Volume, ml - 17

Sensitiveness to Friction

Mallet Test (Expressed as percentage)

Anvil	Mallet	
	Boxwood	Steel
Yorkstone	0	100
Hardwood	0	0
Softwood	0	0
Mild Steel	0	50
Naval Brass	0	50
Aluminium Bronze	Not tested	

Sensitiveness to Frictional Impact

Glancing Blow Test (Minimum Ignition Energy), joule.

a. Steel on Steel	Greater than 11.0
b. Brass on Steel	Greater than 11.0
c. Steel on Bakelised Cloth	Greater than 11.0
d. Brass on Bakelised Cloth	Greater than 11.0

Temperature of Ignition

221°C

Ignition by Flash

Fails to ignite.

Behaviour on Inflammation

Ignites and supports train steadily throughout.

Ignition by Electric Spark

Ignition at 4.5 joule but not at 0.45 joule.

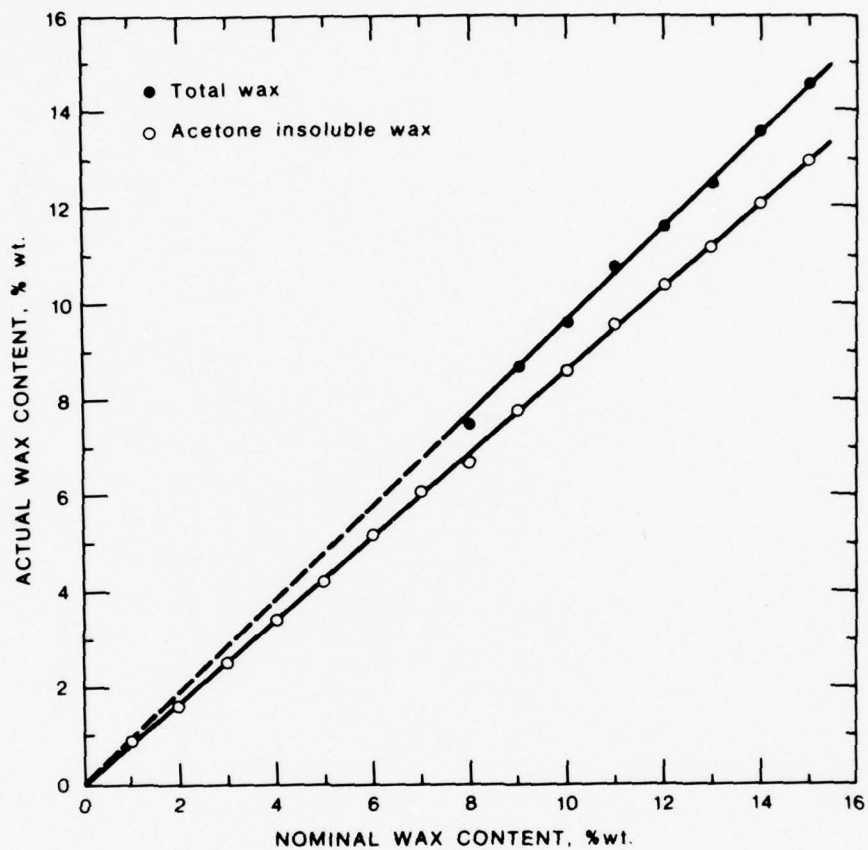
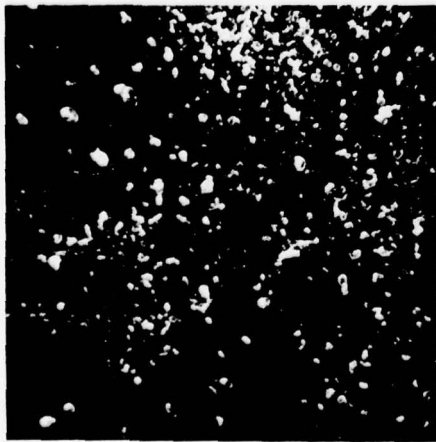
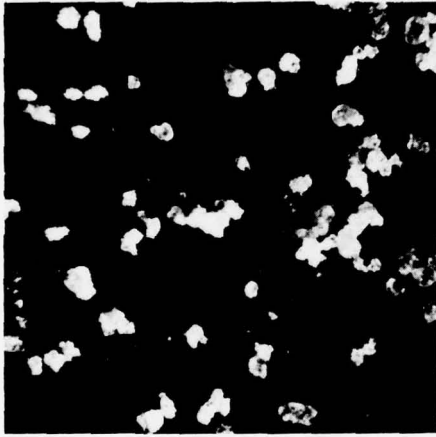


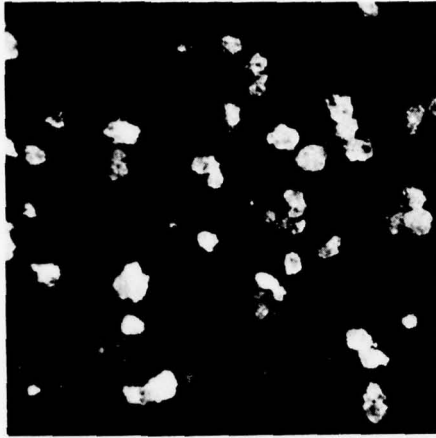
FIG. 1 - Analysis of wax content in RDX/polyethylene wax compositions.



RDX GRADE 1A



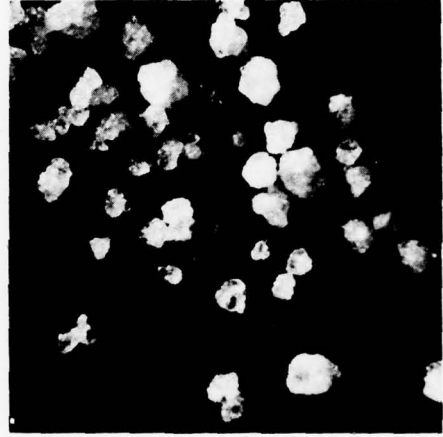
1% WAX



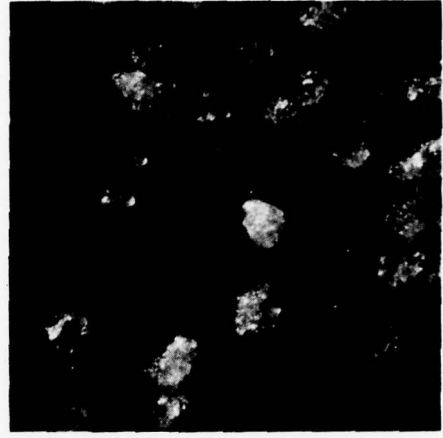
2% WAX



4% WAX



8% WAX



12% WAX

X 13-3

FIG. 2 - Photomicrographs of RDX/polyethylene wax compositions.

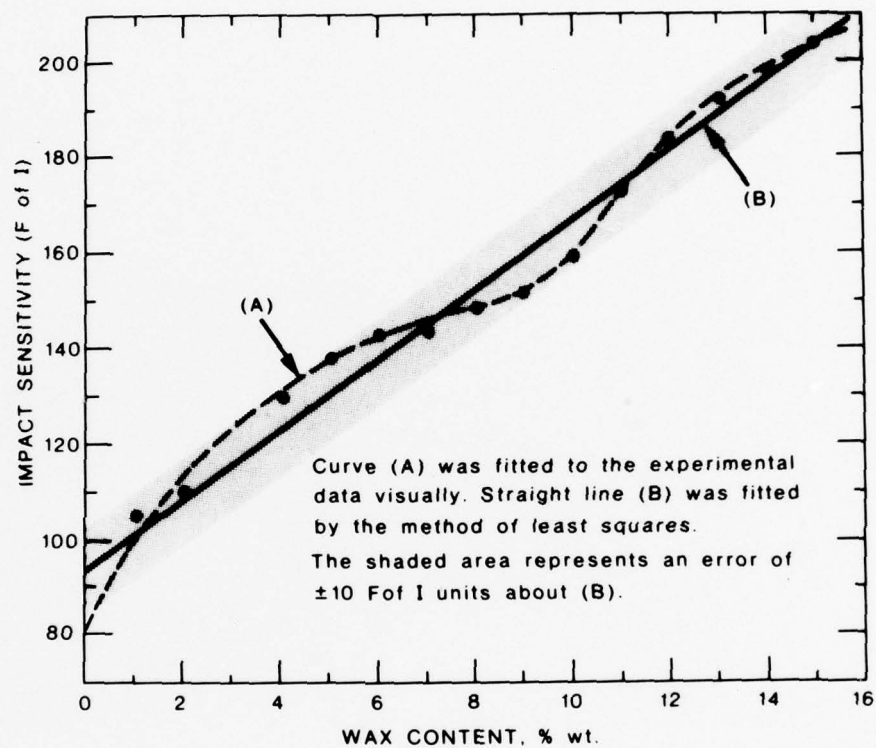


FIG. 3 - Impact sensitivity of RDX/polyethylene wax compositions.

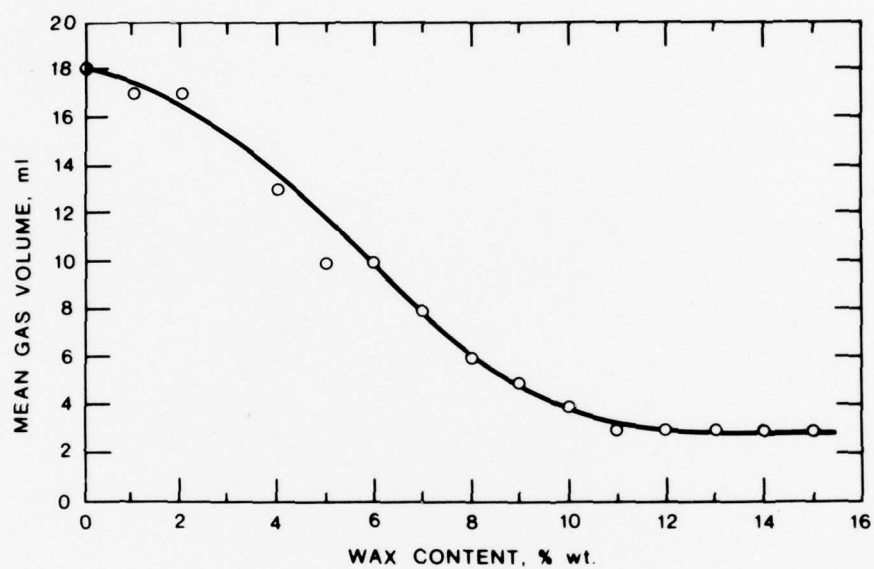


FIG. 4 - Gas evolution during Rotter impact testing of RDX/polyethylene wax compositions.

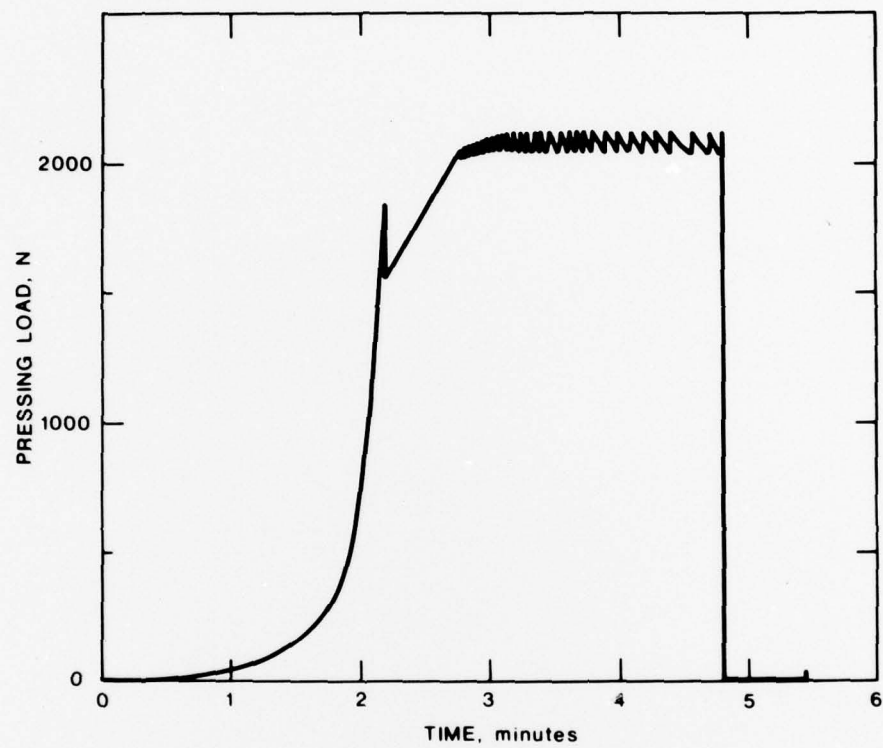


FIG. 5 - Typical load/time profile for the compaction of RDX/polyethylene wax 92.5 : 7.5.

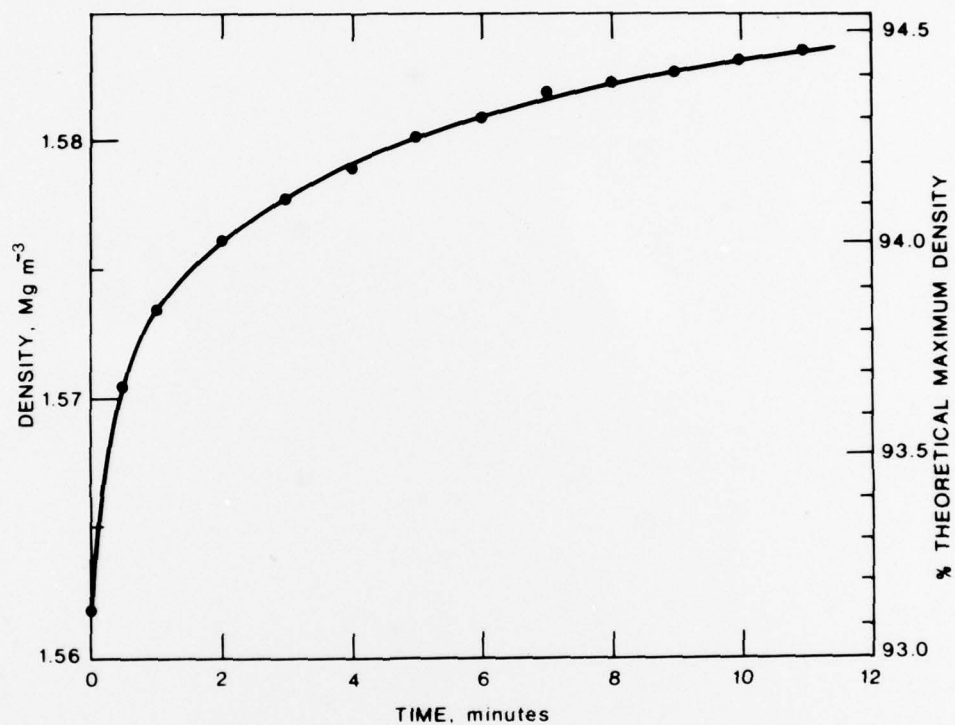


FIG. 6 - Density of RDX/polyethylene wax 92.5 : 7.5, pressed in a half-inch mould with a dead load of 3.97 kN, as a function of time.

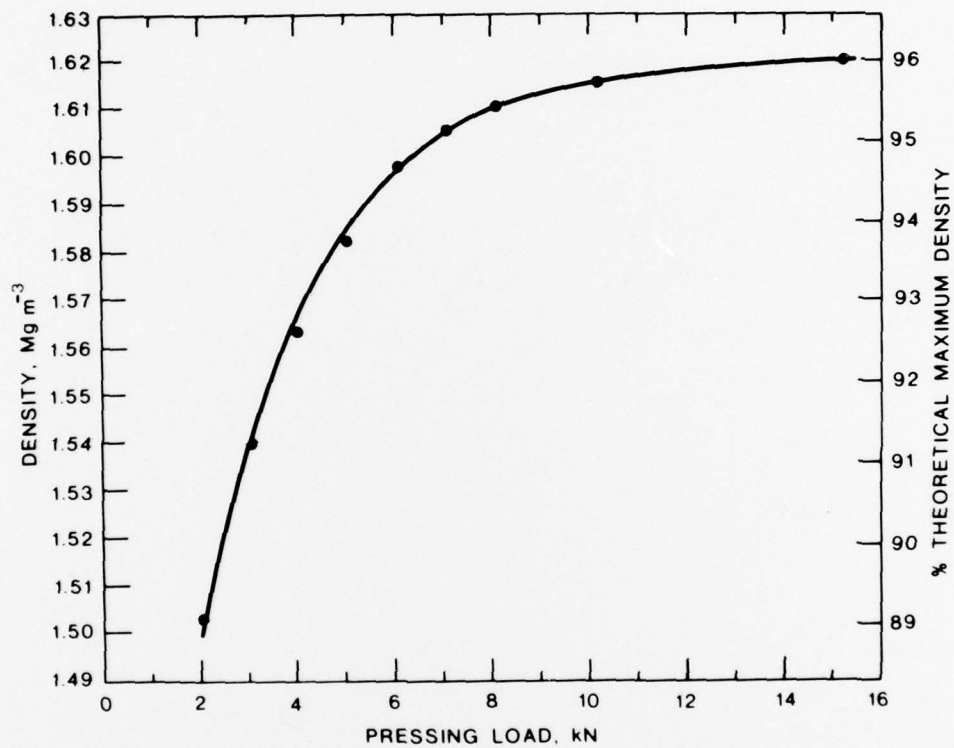


FIG. 7 - Density of RDX/polyethylene wax 92.5 : 7.5, pressed in a half-inch mould with a dwell-time of 2 minutes, as a function of pressing load.

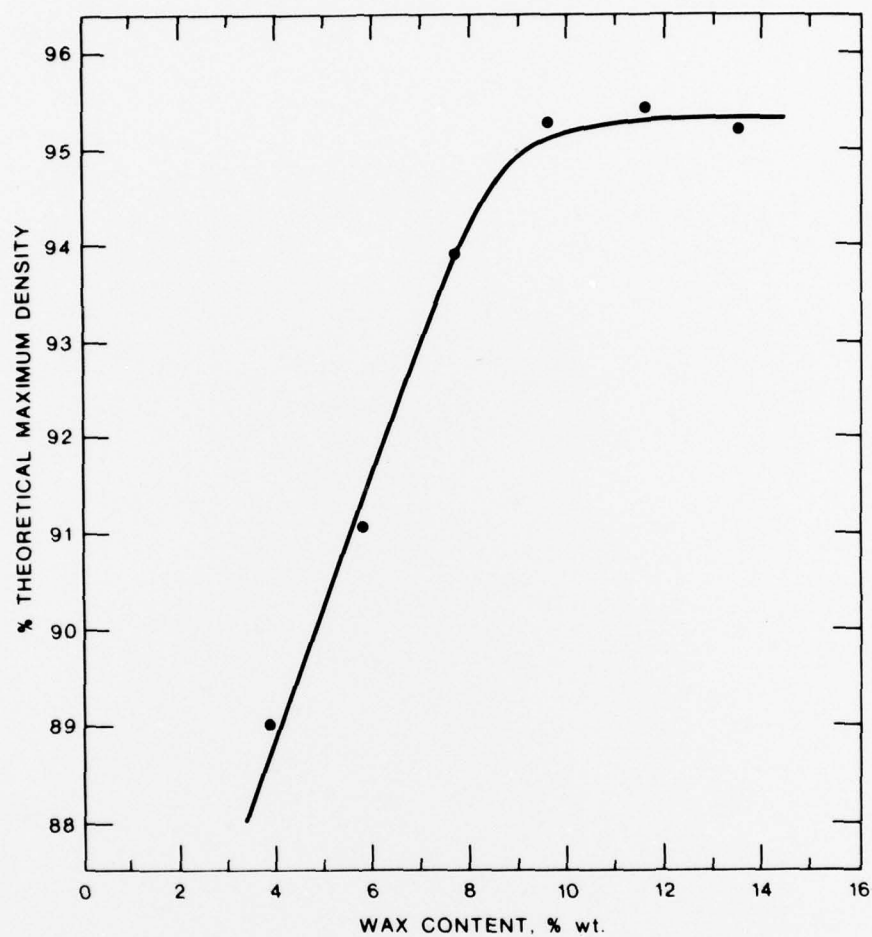


FIG. 8 - Density of RDX/polyethylene wax, pressed in a half-inch mould with a pressing load of 4.90 kN and a dwell-time of 2 minutes, as a function of wax content.

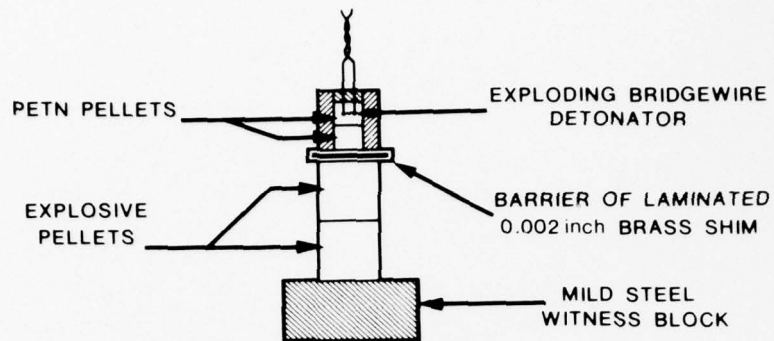


FIG. 9 - Gap test assembly for measurement of shock sensitivity.

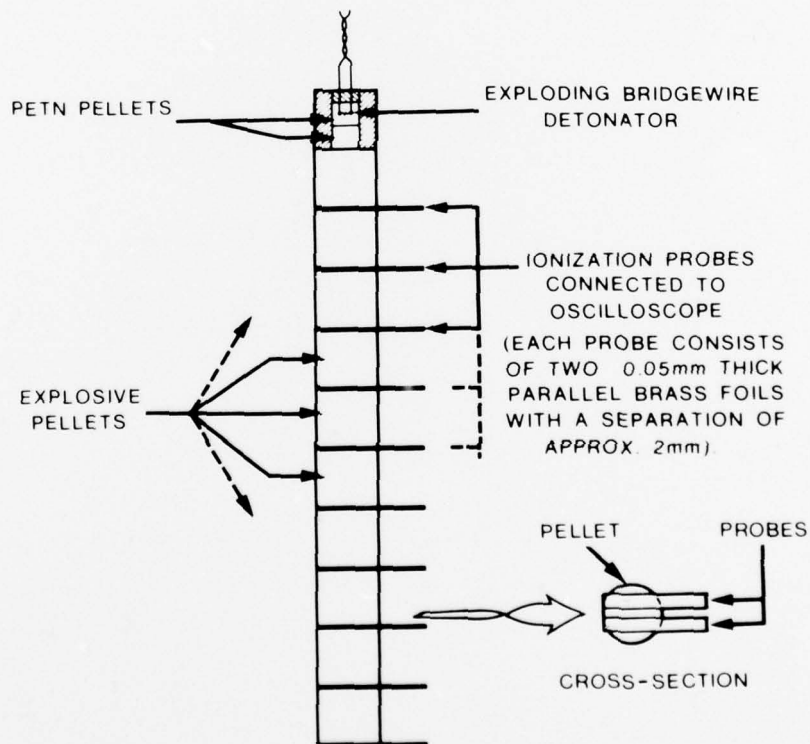


FIG. 10 - Assembly for measurement of velocity of detonation.

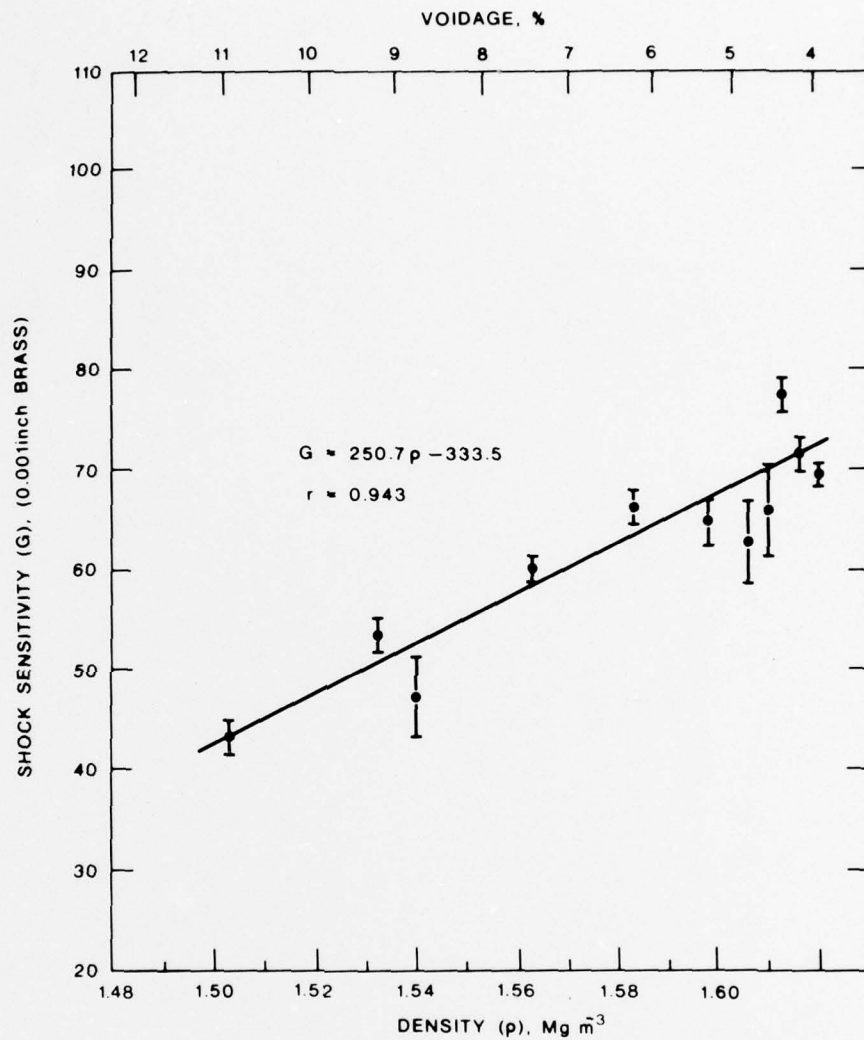


FIG. 11 - Shock sensitivity of RDX/polyethylene wax 92.5 : 7.5 as a function of density.

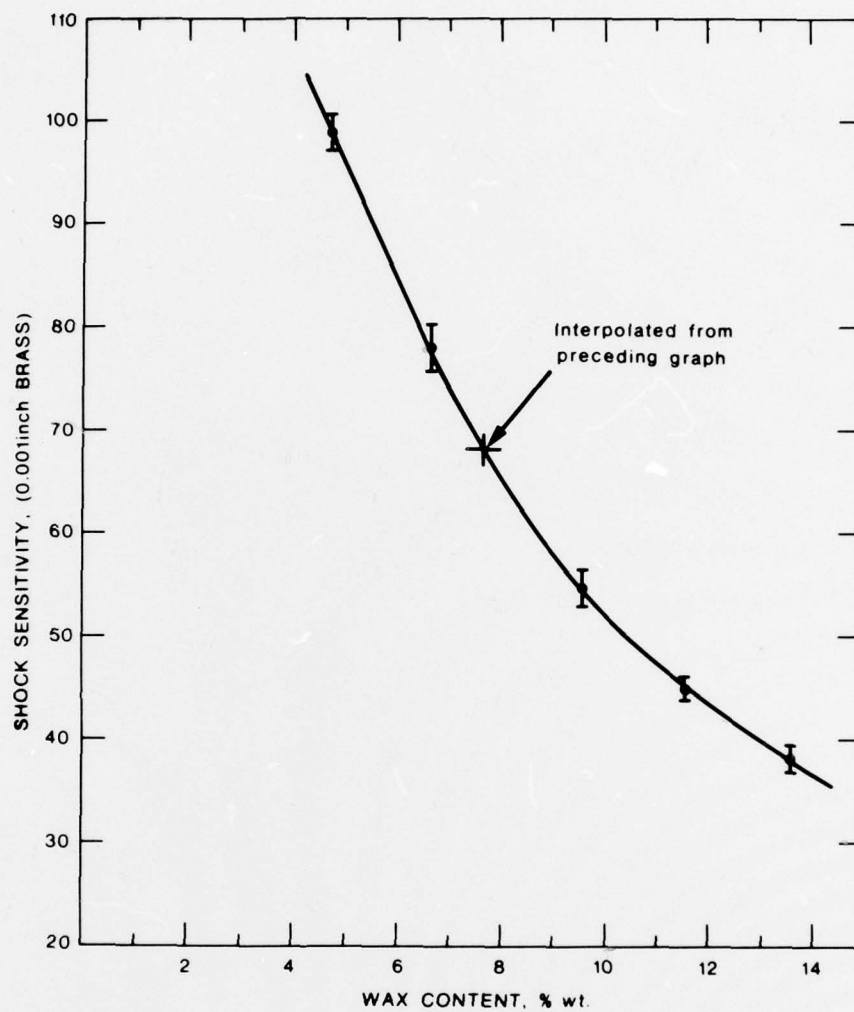


FIG. 12 - Shock sensitivity of RDX/polyethylene wax, pressed to 95.2% theoretical maximum density as a function of wax content.

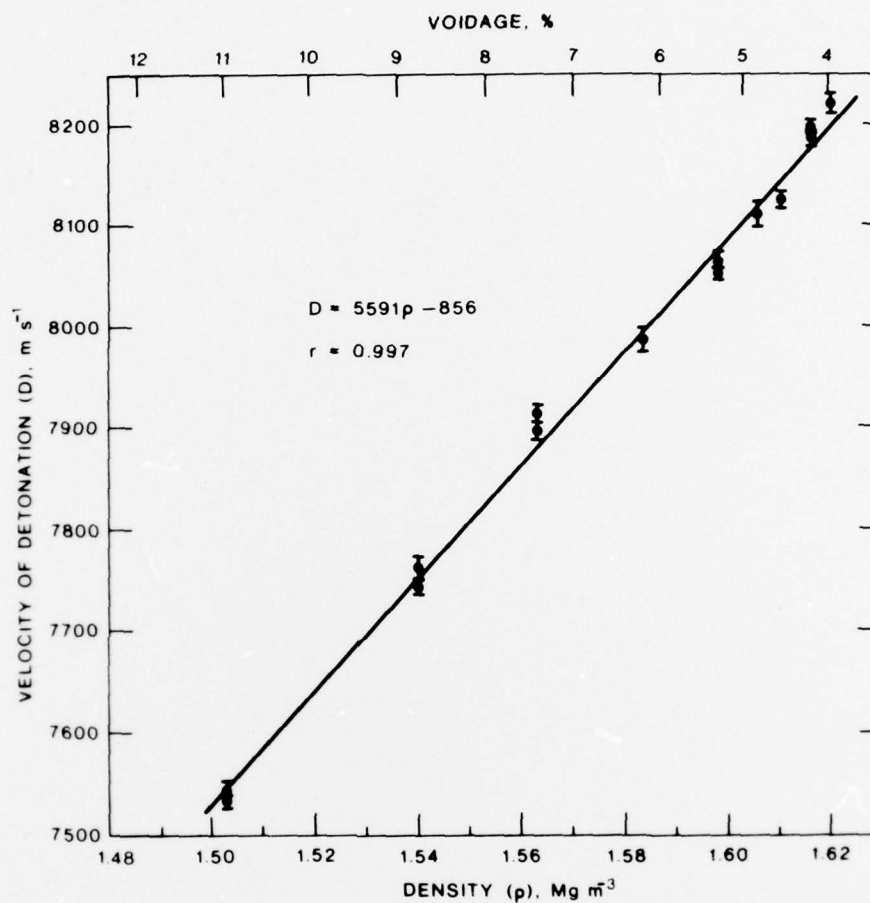


FIG. 13 - Velocity of detonation of RDX/polyethylene wax 92.5 : 7.5 as a function of density.

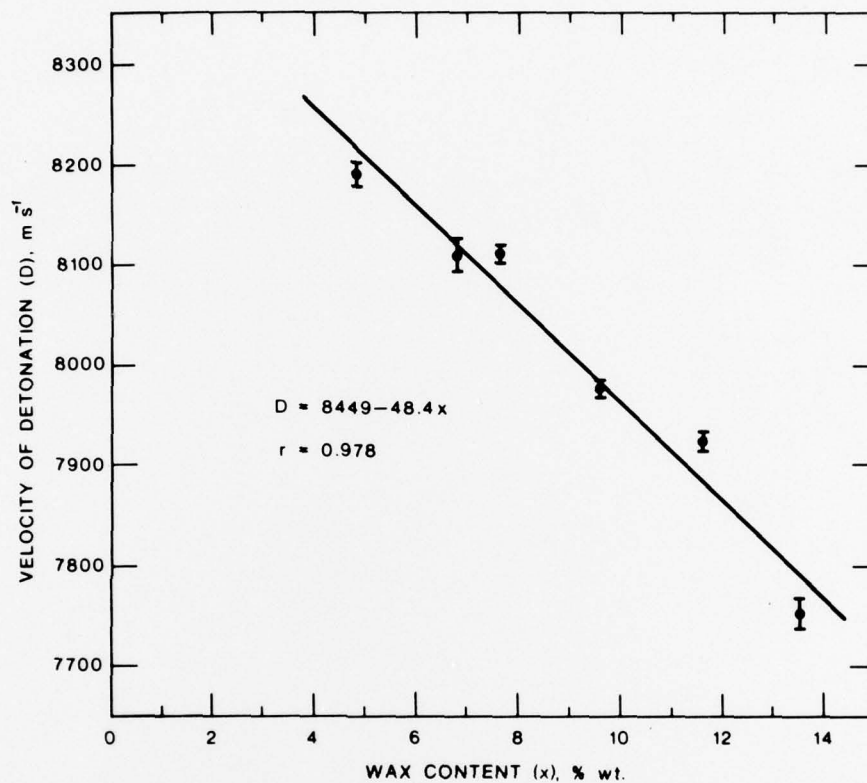


FIG. 14 - Velocity of detonation of RDX/polyethylene wax, pressed to 95.2% theoretical maximum density, as a function of wax content.

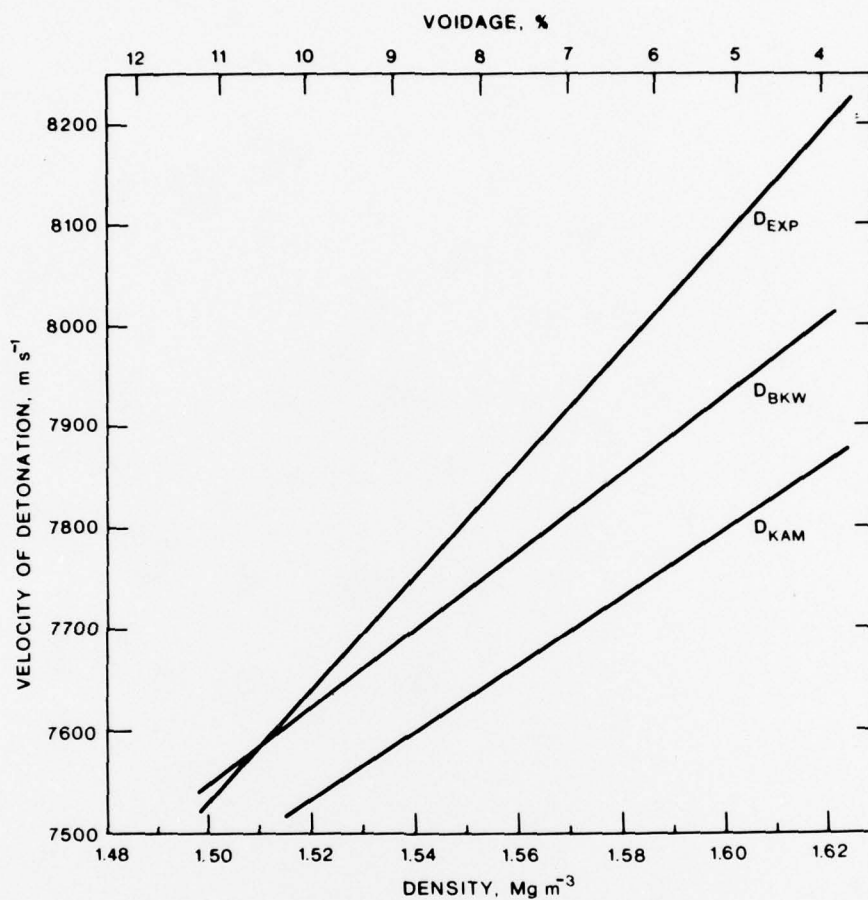


FIG. 15 - Variation with density of the experimental values of velocity of detonation of RDX/polyethylene wax 92.5 : 7.5, and comparison with the values predicted by the Kamlet and BKW codes.

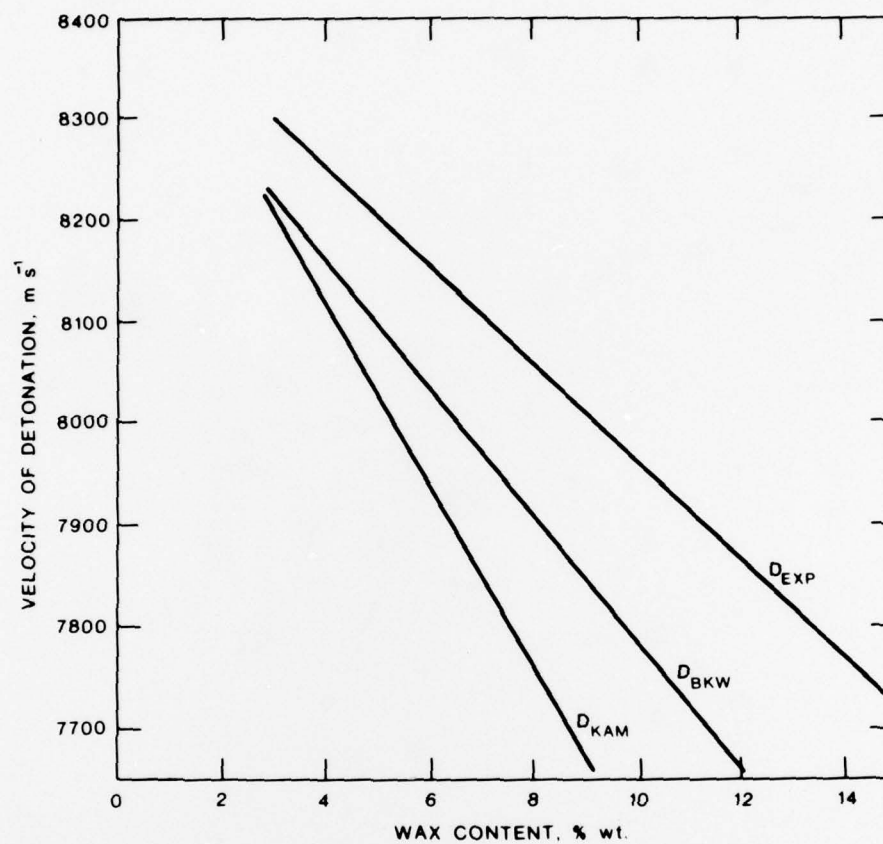


FIG. 16 - Variation with wax content of the experimental values of velocity of detonation of RDX/polyethylene wax, and comparison with the values predicted by the Kamlet and BKW codes.

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