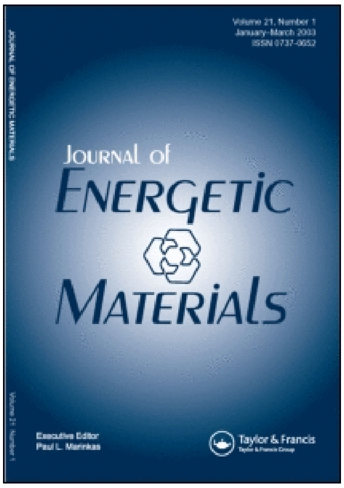


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Pourability enhancement of petn explosive powders

Marcia Dee Vannet[a]; George L. Ball[a]
[a] MRC-Mound, Miamisburg, Ohio

To cite this Article Vannet, Marcia Dee and Ball, George L.(1987) 'Pourability enhancement of petn explosive powders', Journal of Energetic Materials, 5: 1, 35 — 55

To link to this Article: DOI: 10.1080/07370658708012348

URL: http://dx.doi.org/10.1080/07370658708012348

POURABILITY ENHANCEMENT OF PETN EXPLOSIVE POWDERS

Marcia Dee Vannet and George L. Ball

MRC-Mound

Miamisburg, Ohio 45342

ABSTRACT

Manufacture of precision detonators requires the pelletizing of very fine, organic, crystalline explosive powders. Production of pellets in automatic machines within critical dimensional and weight tolerances requires that the powders pour uniformly into die cavities. The pellets must be able to be initiated with low energy and have a predictable energy output. Modifications to needle-like crystalline PETN explosive powders to make them pourable were introduced by the application of about 80 A thick polymeric coatings to the individual crystals, followed by a controlled agglomeration into a spherical prill. Microencapsulation techniques provided the key to achieving the result using less than 0.5 wt. % coating (an order of magnitude less coating than in usual PBX systems). These coatings did not appreciably alter the energy required to initiate and significantly increased the strength of the pellets. A key point demonstrated, which may be translated to other applications, was that powders that exhibit performance based on physical characteristics could have their handling and strength properties tailored with little change in their primary function.

Journal of Energetic Materials vol. 5, 35-55 (1987)

Published in 1987 by Dowden, Brodman & Devine, Inc.

1. INTRODUCTION

The chemical energy for precision detonators is supplied by compacted, fine, organic, crystalline explosive powders. The powders may be compacted into high (near theoretical) density pellets or lower (ca. half theoretical) density in-place moldings - depending on the specific application. The performance of the detonator is dependent upon the compacted density, surface area, and particle size and distribution of the powder, in addition to its specific chemical composition. In essence, the physical characteristics of the powder are as important as its chemical composition relative to desired performance as an explosive.

Both the actual value and uniformity of the density of the moldings or pellets are critical to their desired performance. This performance is reflected in both the required initiation and the developed output energies. Generally the lower the density, the less the energy required to initiate. Powder surface area also has an effect on the ability to initiate, but the degree and nature of this effect depends on the method of initiation. Initiation methods include hot wires, exploding bridge wires, and slapper impact, which provide the introduction of thermal and/or mechanical energy to the compacted powder over a short interval (nanoseconds).

Typically, the desired crystalline explosive powders are needle-like in shape. Consequently, they do not pour (flow through a funnel and distribute within an irregular cavity) well. They also are very fine (3-30 μm effective length), non-conductive powders that are subject to electrostatic forces and dispersion in air. Conductive and pour-enhancing additives, such as graphite and stearates, are routinely added to explosive powders. These additives improve their handling characteristics (reduced floating and sticking to the surfaces of containers, for instance), but do not make the powders pourable enough for use in automatic pelleting machines.

Pourable, and even castable or melt-extrudable, explosives can be produced by agglomerating and/or coating energetic powders with plastics. These are referred to as plastic-bonded explosives (PBX) and generally contain ~4 wt% polymer, or more. The pourability is provided by the rounded plastic surfaces inherent in the solidification of plastics from the melt or solution, and by the generation of larger particles having weights that overcome electrostatic forces and air turbulence. These coatings are generally not uniform in thickness and do decrease the sensitivity of the explosives to initiation. (In fact when reduction of initiation or propagation sensitivity is desired, plastic bonding provides that effect.)

The integrity of a molding or a pellet used in a precision detonator is necessary for high reliability performance. Any internal fractures, or surface or interface discontinuities could prevent detonation propagation, or even initiation, of the compacted energetic powder (especially if an interface between a bridgewire and the explosive is violated). Thus it is important that the compacted powder have strength to maintain the integrity of the molding, both initially and after exposure to various thermal, mechanical shock, vibration, and chemical environments.

2. SUMMARY

This report presents the results of a program to provide both improved pourability to dry explosive powders and increased strength to moldings prepared from these powders. The primary driving force was to make available powders that could be formed in automatic pelleting machines and then handled by robotic manipulators. Initiation sensitivity, propagation, and timing characteristics of the explosives were to be maintained.

The technique proven viable incorporated the application of very thin plastic coatings to each of the individual explosive crystals, and then the agglomeration of these coated crystals into larger, more spherical particles (prills) which pour readily. The coating and prilling were achieved during suspension of the powders in a liquid medium which had no measurable effect on the structure, chemistry, particle size or surface area of the organic crystals. The process that was developed incorporated features from microencapsulation, prilling, and plastic bonding technologies.

Other approaches were considered and may eventually prove useful, such as blending in additives or recrystallization into more spherical powders.

3. TECHNICAL DISCUSSION

The experimental program consisted of the tailoring of explosive powders with polymeric materials using developed processes that incorporated features from plastic bonding, microencapsulation and prilling technologies. The tailored explosives were then characterized for pourability; form, size, and appearance as powders; and strength and retention of explosive properties as pellets.

The initial development was done in 1-5 g batches in laboratory glassware, but then was scaled to ~100 g batches in a pilot 10-L vessel. The developed formulations and techniques are expected to be readily scalable to 1 kg batches.

3.1 Materials

The basic materials of interest were fine (3-30 μm), dry, explosive crystals of high purity. The crystals were coated with thermoplastic (soluble) high molecular weight polymers from solution during suspension in a liquid nonsolvent medium. Surfactants were used to facilitate the coating operation, required especially because of the very low weight of polymer addition.

3.1.1 Explosive Powders

The explosive powders of PETN (pentaerythritol tetranitrate) ranging in surface areas from 4,000 to 12,000 cm^2/g (measured by Fisher subsieve sizer) received the greatest emphasis. However, the techniques were also demonstrated on other explosive materials, which had significantly different solubility and initiation sensitivity characteristics. Demonstration of the developed techniques on this set of explosives 1) resolved any concerns over the effect of the organic solvents on the organic crystals and 2) provided a range of initiation sensitivities to better define the desired lack of effect of thin polymeric coatings on initiation sensitivity. One concern in using organic solvents in conjunction with the organic crystals, of course, was the potential for change in crystal morphology, particle size and/or surface area. Such changes could not be tolerated for precision detonator applications.

Crystal morphology and surface area were also examined. The specific types of PETN crystals (two) and their surface areas are shown in Table 1. The two types of crystals were examined because they are of interest for

TABLE 1

Differing Crystal Morphologies and a Range of Surface Areas of PETN Explosive Powders Were Examined to Define the Boundaries of the Process

Identification	Surface Area (cm^2/g)	Crystal Shape
ER 7477	4000	needle
ER 7256	5000	needle
ER 7478	7000	needle
ER 7479	12000	needle
ER 7487	5000	flower

detonator applications and they represent morphological differences that may cause differing sensitivities to solvents or other environments. The various surface areas were examined because of their application interest and also to demonstrate the available range over which angstrom-thick coatings could be applied; i.e., application of the same weight of polymer to a 12,000 cm^2/g versus a 4,000 cm^2/g surface area would result in a coating of one-third the thickness.

3.1.2 Polymeric Coatings and Surfactants

The plastic coating materials were selected based on their historical acceptability and compatibility in PBX systems used in earlier detonators. These criteria were used after it was found, unexpectedly, that any soluble polymer would work independent of its solubility parameter. Polymers, ranging from highly polar vinyl acetate to low surface energy fluorinated vinyls, were investigated. This independence was achieved by using ethanol as the surfactant.

The thermoplastic polymers examined are shown in Table 2. The ethyl cellulose was used originally to demonstrate the coating concept since it had

TABLE 2

A Wide Range of Thermoplastic Polymers Was Examined and Found Acceptable for Microencapsulation of the Explosive Powders

Ethyl Cellulose
Polystyrene
Polyvinylacetate
Polymethylmethacrylate
Vinylchloride/trifluorochloroethylene copolymer (FPC-461)

well established microencapsulating characteristics. The other polymers were examined to demonstrate the latitude available in selecting the coating material independent of their inherent wetting abilities (solubility parameter).

The vinylchloride/trifluoro-chloroethylene (FPC-461) represented a low surface energy polymer. The density of FPC-461 very closely matches that of PETN (PETN - 1.78 g/cc, FPC-461 - 1.7 g/cc). It was of prime interest, however, because of its established performance in plastic bonded explosives (PBX) - which is why it was selected for most of the scaled up experimental effort.

The crosslinkable polymer systems of urea-formaldehyde and gelatin were also shown to be usable for microencapsulation of PETN explosive powders. However, they require a more complex process and thus were not pursued.

3.1.3 Liquid Medium

Liquids performed three primary functions: first, to disperse and suspend the explosive crystals so they could be individually coated; second, to dissolve and dilute the polymers which are to form the coatings; and third, to act as a surfactant.

The primary suspending medium was deionized water. It was highly advantageous because of the insolubility of organic crystals in it, the miscibility of solvents in it, its purity, its freedom from industrial hygiene problems, and its ready availability. Its high thermal capacity also could have a stabilizing effect on the temperature, thus forcing a more consistent precipitation of the polymer.

The solvents used in the process were selected for 1) their lack of effect on the energetic crystals, 2) their solvency power for the specific polymer, 3) their ability to be eliminated from the final product, and 4) their freedom from industrial hygiene problems. The specific solvents used to dissolve and dilute the polymers will be discussed with the results on specific coating processes.

The surfactant provided the mechanism for the energetic crystals to attract the polymer (in solution) to deposit on the crystals, rather than to have the polymer precipitate as useless spheres. Although surfactants such as polyvinylalcohols were examined and found to be useful, it was discovered that ethyl alcohol, commonly used in the processing of explosive powders, served the function very well. Since it was desirable that new and/or different materials not be incorporated into the system, this result was most fortuitous.

3.2 Processes

The developed process contained three major stages: first, the application of a coating in the 100 A thickness range to the individual explosive crystals; second, a controlled agglomeration of the coated crystals into much larger spherical particles; and third, the separation of these particles from a liquid medium into the form of a dry flowable powder. The difference between this process and plastic-bonding of explosives will become evident and is an important distinction.

3.2.1 Coating (microencapsulation)

The key to achieving the overall desired result lies in the coating process. In essence, a set of conditions was determined that 1) keep the PETN crystals (density 1.78 g/cc) suspended, and 2) favor deposition of a uniformly thin coating onto each of the individual crystals. The process is outlined in Figure 1.

The process consists of 1) dispersing a small quantity of PETN powder into ethanol/water (1:1 v/v) (typically 4 g in 30 mL), 2) diluting the dispersion with water (typically 10 times the solvent), 3) vigorous agitation of the mixture, and 4) a slow (dropwise) addition of a dilute solution of a polymer (0.02 g in 50 mL) into the dispersion.

It is this starved addition of a polymer at a very low concentration to the individually suspended crystals that forces thin uniform coatings in the range of 20 to 800 A (calculated based on an assumed uniform distribution over a measured surface area), and is what distinguishes the technique from plastic-bonding where crystals are added into a concentrated polymer solution. The angstrom thicknesses are the result of adding 0.5 to 20 wt. % of polymer to powders having surface areas of ~5000 cm^2/g. Additions greater than 1% were done only for completeness of the study.

The final steps to this coating process are the removal of the solvent and separation of the coated crystals from the liquid medium. The solvent (for the polymer) was removed by heating the solution to 45°C and letting it

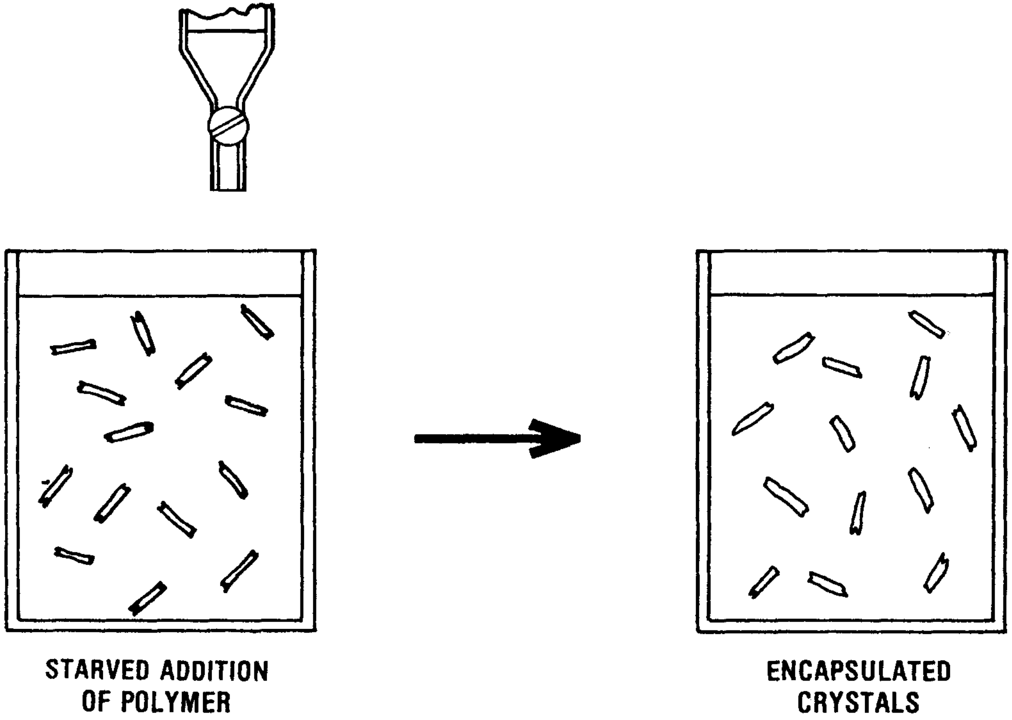


Figure 1
Microencapsulation techniques extend PBX technology by introducing control over the coating of individual crystals.

boil off. The coated crystals were then separated by filtering, washing, and air drying.

Except to facilitate solvation of polymers prior to the coating of crystals or to evaporate the solvent as noted just above, the majority of the experimental work was done at room temperature (~25°C). Addition time and concentration of the polymer solutions were controlled and determined to be critical parameters in the microencapsulation and prilling processes.

It is important to note that, while microencapsulation technologies were used in the processes, total and integral encapsulation, per se, was not deemed critical.

A typical process formulation and addition rates are given in Table 3. The coating process was scaled up to 100 g batches from 4 g batches in a 10 L reaction vessel available for processing explosives. The process was shown to be scalable over this two-order-of-magnitude range.

TABLE 3

Process Formulation and Parameters for Microcoating Illustrate the Starved Addition Which is Key to the Process

PETN	100 g	
Water	4000 g	A
Ethanol	400 g*	
Dichloromethane	500 mL	
FPC 461**	0.5 g	B
Agitator speed (of A)	300 rpm	
Polymer addition rate	1 L/hr	(B into A)

---

*For batches using ER 7479, 600 grams of ethanol were used.

**For batches using ER 7256, which were preliminary, ethyl cellulose was the plastic used.

3.2.2 Prilling (Controlled Agglomeration)

The prilling process consists of forcing the agglomeration of the coated crystals (which do not flow much better than the uncoated crystals) into more spherical particles. Increasing the size and weight of the particles is also important to generate heavier particles which can overcome electrostatic forces.

Having as a starting point crystals coated with a soluble plastic, agglomeration is achieved by sticking the crystals together under controlled conditions. This process step is illustrated in Figure 2. First the coated crystals are redispersed into an alcohol/water medium. This time, however, a very low, and critical, level of a solvent is added dropwise to tackify the surfaces of the plastic coating. This gives them the ability to stick together. The crystals are formed into larger, more spherical arrays by introducing a specific level of turbulence to the dispersion. The turbulence must be strong enough to create the arrays, but moderated so that the agglomerates are not fractured. As the agglomerates progressively increase in size the agitation can be reduced to stimulate even greater growth. The experimental conditions are shown in Table 4.

TABLE 4

A Typical Formulation for Prilling Illustrates the 100/1 Dilution of the Active Solvent

Coated PETN	100 g	C
Water	4200 g	
Ethanol	400 g	
Toluene	50 g	D
Agitator speed (of C)		300 rpm
Addition rate		5 g/min (D into C)

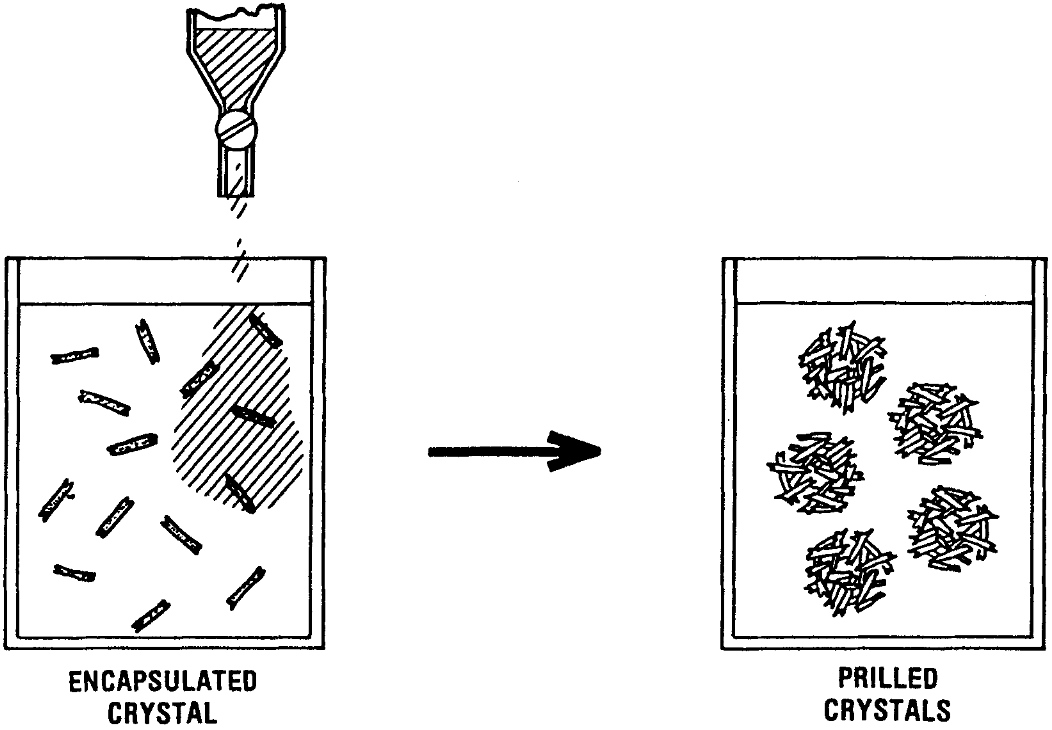


Figure 2
Prilling of microencapsulated crystals increases powder particle size while retaining crystal surface area.

3.2.3 Stabilization and Separation

A final and a most important part of the manufacturing process was the extraction of the prilled powders from their liquid medium, by filtering, washing with water, and drying. Freeze-drying, however, was shown to have a major advantage over oven-drying, relative to pourability. It was originally anticipated that the solvent would need to be boiled off before any filtering was attempted, but this was found to be unnecessary.

Keeping the prilled powder very dry was also shown to be necessary to maintain good pourability. Day-to-day changes in humidity (in the Dayton area) were sufficient to radically change the pourability of the powders. Safety precautions dictate relative humidity of at least 40%, so resolution of this problem is required. The cause of this effect, especially with the fluorinated polymer coatings is presently unknown.

3.3 Physical Characterization

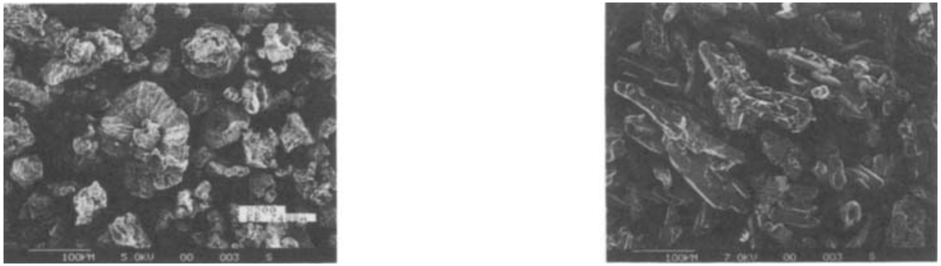
Having defined the materials and processes to achieve the candidate energetic prills, the prills were evaluated both quantitatively and subjectively for performance, both as powders and as molded pellets. Characterization included appearance, pourability, strength and environmental effects.

3.3.1 Appearance, Form, Size and Density

PETN exists in two basic crystal morphologies. The most common is a needle-like crystal, which accounts for the poor pourability of the powder. The other crystal type is rounder, and sometimes looks like a flower. Scanning electron microscope (SEM) photographs of these two crystals are shown in Figure 3. It is not possible to observe the polymer coating in SEM

N05K - uncoated

N05K - 0.5% coating



F05K - uncoated

F05K - 0.5% coating

Figure 3
Scanning electron microscope photographs show that the two crystal types of PETN are not altered by microencapsulation.

photographs, other than as an apparent slight rounding of the edges of the crystals as shown.

The prilled, microencapsulated PETN powders are made up of agglomerates of the coated crystals, and are basically spherical. Visually, and under low magnification, these particles resemble a typical PBX powder (with ~5% polymer). However, the SEM photographs shown in Figure 4 reveal the difference. The PBX particle shows large smooth areas, which are excess polymer. The prilled, microencapsulated particle has no such smooth areas, but rather shows only the PETN needles.

The bulk densities of the PETN powders examined are very low, which is another factor that affects their pourability. Bulk density measurements made on the prilled, microencapsulated powders show that prilling increases the bulk density, which helps to improve the pourability. The bulk density data are presented in Table 5 [1].

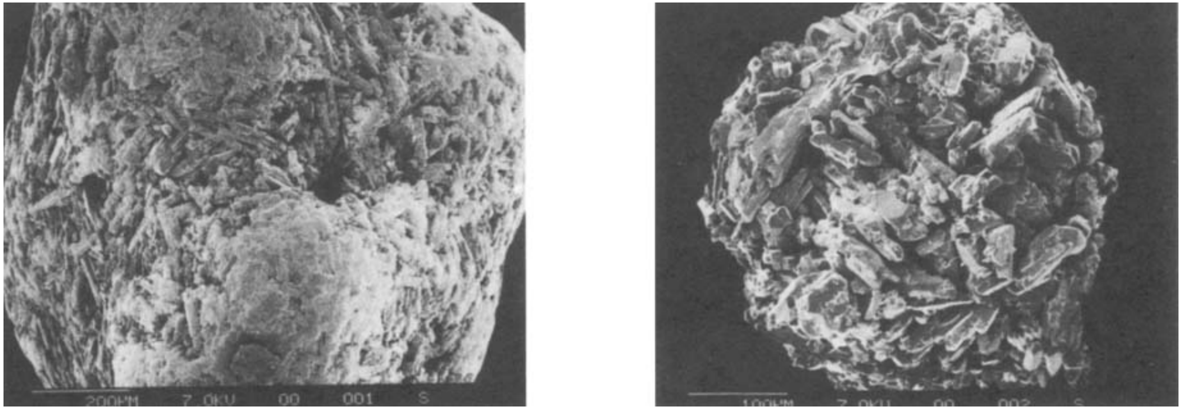
TABLE 5

Bulk Density Data Show that Prilling Increases the Bulk Density of the Particles, Which is Necessary for Pourability

Powder	Bulk Density (Starting Material) g/cm^3	Bulk Density (Prilled) g/cm^3
ER 7477	0.19	0.33
ER 7478	0.13	0.26
ER 7479	0.18	0.27
ER 7487	0.38	0.42

3.3.2 Pourability

Needle-like PETN will not pour through a funnel and cannot be made to flow in an automatic pelleting machine. Flower-like PETN has somewhat better



Typical PBX - 3.5% binder

Prilled microencapsulated crystals - 0.5% binder

Figure 4
Photographs of 0.5% and 3.5% level binder on PETN powder illustrate the efficient use of binder achieved by microencapsulation versus a PBX technique.

pourability, but is still not satisfactory for automatic pressing. Microencapsulation of PETN does improve the pourability to a slight degree, but not sufficiently for automatic pelleting. Prilling, or agglomerating, significantly increases the pourability of both crystal forms of PETN.

Pourability measurements were quantified using the Hall flowmeter [2]. It was necessary to make a funnel with a larger diameter hole (1 cm) in order to make these measurements, since the apparatus was designed for metal powders. It is interesting that flow rates of about 3 g/sec were achieved for all of the prilled powders, regardless of the surface area or shape of the original material. Flow rates for all of the unprilled powders were 0 g/sec.

3.3.3 Strength

Initial strength measurements were performed on molded pellets in a qualitative (pass/fail) manner. The test consisted of molding ~1/8 in diameter by 1/16 in thick pellets in a polished steel compression mold. The pellets were then ejected from the mold through a 1 in sleeve with a pin type ejector. A specific amount (0.10 g) of powder was used for each molding and the powder was compressed to 90% of theoretical density.

Pellets made from untreated PETN powders, when compacted and then extracted in this manner, break up into thin disks or small pieces. In essence they cannot survive the extractive forces (which were not quantified). Pellets coated with as little as 0.5% of polymer, however, survived the extraction and formed integral pellets that could not be fractured even when subjected to being picked at with a sharp spatula tip.

Another rather subjective, but quantifiable, test was developed to illustrate the reduced friability introduced by the thin polymeric coatings.

The test consisted of first preparing pellets as above, but not using the sleeve for ejection (so integral pellets of all types could be generated). These pellets were weighed and then subjected to a tumbling motion in a round-bottom flask, by means of a magnetic stirrer. A convenient exposure time, enough to demonstrate differences, was empirically derived to be 30 min. Following the tumbling, the three largest fragments were weighed, and finally the percent weight retained was calculated.

Pellets made from powders ranging in surface area from 4000 to 12000 cm^2/g, and containing 0.0 and 0.5% polymer were tested this way. The friability data are presented in Table 6. In all cases, as little as 0.5 % polymer causes a reduction in friability, ranging from 10 to 40 percent. The scatter in the data is due to the lack of reproducibility in experimental conditions.

TABLE 6

The Friability of PETN Pellets can be Reduced With as Little as 0.5 % Plastic Coating Applied to the Powder

	Weight Percent Lost*	
Powder	Coated	Uncoated
ER 7477	9	36
ER 7478	12	16
ER 7479	7	14
ER 7487	6	45

*Portion of pellet lost due to mechanical abrasion during tumbling.

3.3.4 Initiation Threshold

Retention of the initiation sensitivity of the coated prills and of the moldings and pellets made from these prills was an important and determinant factor in the overall development. This retention was what could distinguish these particles from PBX powders that exhibit a significant decrease in sensitivity.

Initiation threshold experiments of the uncoated and coated powders were performed using an experimental slapper detonator. The slapper refers to the use of a small (pinhead size) disk of plastic that initiates detonation by mechanical impact with the pellet. Burst current densities indicating the energy to initiate were measured at -1100 V voltage threshold. Measurements were made on moldings at a density of 1.65 g/cm^3. These results are for a 0.5 wt. % addition of polymer. All of the uncoated powders had burst current densities of 210 GA/m^2, while the microencapsulated materials ranged from 200 to 230 GA/m^2. Within the precision of these tests (± 15%), these values are indistinguishable, although there is more scatter in the data for the coated powders.

4. CONCLUSIONS AND FUTURE WORK

These results demonstrate that microencapsulation and prilling techniques can be used to tailor explosive powders for automatic handling. With as little as 0.5% coating, the strength of molded pellets is increased. Explosive powders that have been microcoated with as little as 0.5 % polymer can be prilled to produce pourable powders that perform satisfactorily in automatic pelleting machines. These improvements in handleability of the PETN powder are possible, while maintaining the ignition sensitivity of the uncoated PETN powder.

Having achieved the primary goal of this effort, it would now be desirable to characterize these powders more completely. Characterization efforts will be directed toward providing more information about the nature of the coating, the thickness of the coating; the weight percent of the coating, and also the surface characteristics of the coated crystals, prills, and the pellets formed from these materials. With a more complete description of these microencapsulated PETN powders, it should be possible to tailor the processes to provide a powder with the desired characteristics for a given application.

5. ACKNOWLEDGEMENTS

We would like to acknowledge the following people for their contributions: G. L. Houston for initiation sensitivity measurements; D. Colman for SEM photographs.

6. REFERENCES

1. ASTM B212-48 "Apparent density of Metal Powders."

2. ASTM B417-64 "Apparent density of non-free flowing Metal Powders."