

Review

Review of Paste Explosives (PEX)

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Abstract

In the early 1970s PEX were being developed in order to produce energetic compounds with a toothpaste-like consistency so that the PEX could be moved into position when arming the warhead. In the late 1990s development work was conducted on PEX for the filling of small-volume microdevices such as microactuators. More recently Cranfield University has just begun research into the development of SPEX. This review outlines the developments in high explosive pastes and concludes with future developments in PEX.

Keywords: Energetic Pastes, Explosives, Paste Explosives, PEX

1 Introduction

Research and development has been carried out on paste explosives (PEX) for many years although very little work has been published in the open literature. Lawrence Livermore National Laboratory (LLNL) has been interested in PEX for some time due to the fact that PEX can be injected into components [1–5]. One of the potential uses of a PEX is in nuclear weapons, here the extrudable PEX could be stored in or near the weapon and then extruded into place when needed [5]. It has been shown that PEX can be prepared nearly void free thus significantly reducing the formation of ‘hot spots’ via impact or shock loading therefore reducing its vulnerability to accident scenarios [6–8].

PEX have also been considered for shaped charges where the explosive and liner need to be in intimate contact. Machined or press-fit explosives tend to have gaps between the liner and the explosive because exact tolerances are very difficult to maintain [9]. PEX can be degassed and injected into the shaped charge without voids resulting in an improved quality of the jet.

2 Pastes

Pastes are used throughout the non-energetics community on a daily basis, from toothpastes, putties and paints to consumables such as starch pastes and mustards. The physical requirements for a paste is the same across the disciplines, that whilst the paste is not under stress it should have the characteristics of a solid but when a stress is applied it should flow like a liquid. This magnitude of stress to induce flow is dependant upon the components and their ratio within the paste.

A paste typically consists of a crystalline or granular material suspended in a fluid. The modality of the crystalline material has an effect on the behaviour of the pastes. This will be discussed in Section 2.1.

Von Holtz [1] describes a paste as having (i) a crystalline phase, (ii) a liquid carrier and (iii) a gelling agent. In order to form a paste the percentage of each ingredient is important and will impact on its rheological behaviour.

2.1 Crystalline Phase

The modality and particle size distribution of the filler plays an important role in the fluid-like properties of the paste. Fine particles with a low size distribution, combined with a low concentration (< 60%) will lead to the particles settling out over time. Therefore there has to be a range of particle sizes to ensure good packing. Teipel [9] mentions several factors that relate to explosive fillers in polymer bonded explosive's (PBX's), gels and pastes, these are:

- mean particle size;
- particle size distribution;
- particle morphology;
- modality;
- packing density;
- chemical nature of particles, i.e. surface interactions.

The rheological behaviour of the material changes as the volume fraction of the dispersed particles increases. Below 2% the behaviour of the mixture follows a Newtonian fluid model however, above 2% mixtures will undergo shear thinning at increased shear rates. Here the mixture transforms from a solid like mixture to a liquid under an increased load with respect to time.

It was noted by Teipel and others [9,10] that the maximum volume fraction ($C_{v,max}$) of monodispersed spheres in a paste range from 0.52 for simple cubic packing, 0.64 for random close packing and 0.74 for face centred cubic packing. Teipel concluded that 0.62 was a reasonable value for the distribution of RDX and ammonium perchlorate in a paste. This value agreed with work conducted at TNO-PML [11] where they looked into the effect of the volume fraction of RDX and ammonium perchlorate on the shear viscosity of a paste containing hydroxyl-terminated polybutadiene (HTPB). The results (see Figure 1) were fitted against a model using 0.62 as the value for the distribution of RDX and ammonium perchlorate in a paste (i.e. $C_{v,max}=0.62$).

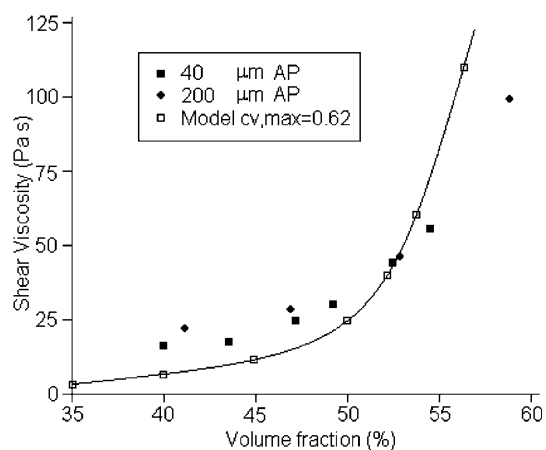


Figure 1. Shear viscosity of monomodal ammonium perchlorate (AP) in HTPB at a constant shear rate of 5 s^{-1} [1].

Teipel also concludes that the choice of the solid filler (i.e. a bimodal or trimodal mixture) together with its mean particle diameter ratio will determine the maximum volume fraction of the paste. A model has been developed for bimodal mixtures with a very small particle size distribution, which predicts the porosity of the particle packing [12].

2.2 Liquid Carrier

Von Holtz [1] and Teipel [9] give details of the ideal requirements for the liquid carrier. These are presented in Table 1.

Using these requirements the LLNL synthesised novel energetic liquids [9]. Examples of these energetic liquids are presented in Table 2.

Table 1. Ideal requirements for the liquid carrier in PBX formulations.

Requirements	Comments
Contributor to the energy output as it will comprise up to 30% v/v of the paste	
Liquid over a large temperature range -54°C to $+70^\circ\text{C}$	This temperature range appears frequently in the criteria required for serviceable munitions
No compatibility issues with any component within the system	
Thermally stable and aid the desensitisation of the explosive filler	This will have an impact on the EMTAP (Energetic Material Testing and Assessment Policy) small scale powder tests during its qualification
Amenable to the formation of a gel structure and have low toxicity, viscosity and vapour pressure	

Table 2. Explosive liquids for use in PEX formulations.

Explosive	Chemical Name and Formula	Density ^{a)} g cm^{-3}	Mol. Wt. g mol^{-1}
BDNPF	Bis(2,2-dinitropropyl)formal $\text{C}_7\text{H}_{12}\text{N}_4\text{O}_{10}$	1.39	312.2
DFE	Bis(2-fluoro-2,2-dinitroethyl) di-fluoroformal $\text{C}_5\text{H}_6\text{N}_4\text{O}_{10}\text{F}_4$	1.67	356.0
FEFO	Bis(2-fluoro-2,2-dinitroethyl)formal $\text{C}_5\text{H}_6\text{N}_4\text{O}_{10}\text{F}_2$	1.607	320.1
MF-1	1-[(2-fluoro-2,2-dinitroethoxy) methoxy]-2,2-dinitropropane $\text{C}_6\text{H}_9\text{N}_4\text{O}_{10}\text{F}$	1.605 ^{b)}	316.1
FM-1	FEFO (23%), MF-1 (52%), BDNPF (25%) $\text{C}_6\text{H}_{9.1}\text{N}_4\text{O}_8\text{F}$	1.509	320.1
TMETN	Trimethylolethane trinitrate $\text{C}_5\text{H}_9\text{N}_3\text{O}_9$	1.47	255.15
TEGDN	Triethylene glycol dinitrate $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_8$	1.335	240.2
EDNP	Ethyl-4,4-dinitropentanoate $\text{C}_7\text{H}_{12}\text{N}_2\text{O}_6$	1.28 ^{c)}	220.0

^{a)} Data obtained from Teipel [9]. ^{b)} Teipel quoted this value as 1.905 g cm^{-3} which is not consistent with other literature values, i.e. 1.605 g cm^{-3} from SciFinder. It was thought that this value from Teipel was a misprint. ^{c)} This value was from data obtained from von Holtz [1].

As shown in Table 2 all liquids have a high percentage of energetic bearing groups and high molecular weights. The densities of all the liquids are lower than most of the explosive fillers, which is surprising because for the formation of gels it is important that the density of the fluid is similar to the density of the filler in order to prevent settling. However, other additives can be included to minimise this effect.

It has also been suggested that polymeric fluids can be used as the liquid phase for the suspension of the energetic filler. This would be similar to the production of castable PBXs whereby the pre-polymers are loaded with up to 88% filler (percentage calculations have been based

on w/w unless otherwise stated) before the addition of a cross-linking agent. As mentioned earlier the quantity of filler required to make a paste is $>60\%$, therefore current pre-polymers would be able to cope with the loading. An issue associated with loading of polymers with fillers is the rapid increase in viscosity, which in turn would affect the shear rate required to move the paste.

Systems that currently use polymers as the fluid phase appear to be restricted to propellant systems. Butyl rubber (15%) has been used to carry NH_4ClO_4 [13] and polydiene rubber (20%) has also been used as the liquid phase for NH_4ClO_4 [14].

Non-energetic liquids such as oils still provide energy by way of being a fuel. Mineral oil ($\sim 5\%$) was added to NH_4NO_3 to produce an Ammonium nitrate fuel oil (ANFO) paste [15]. An improvised paste was produced by the addition of mineral oil (200 ml) to 0.55 kg of Composition 4 (Comp 4, RDX plastic explosive). This had the effect of decreasing the percentage of RDX from 91 to 69% and increasing the oil percentage from 1.6 to 25.4%.

2.3 Gelling Agent

The third requirement for a PEX is the inclusion of a gelling agent. Two approaches have been considered [9] firstly colloidal particles and secondly polymer viscosity modifiers. The former rely on the formation of hydrogen bonding between particles, an example of such particles is fumed silicon dioxide used by von Holtz [1]. The fumed silica particles have a chain-like morphology and when introduced into a fluid a three-dimensional network is formed. This network traps the liquid and increases the viscosity of the composition, leading to an increase in the shear rate to induce flow in the composition. The particles can be obtained in a variety of densities and usually have a large surface area. Applications of fumed silica as a viscosity modifier include fillers for rubbers, coatings, adhesives, cement, paints and cosmetics [16–18].

Examples of polymer viscosity modifiers include ones prepared from OH groups containing acrylic polymers and/or polyesters. An example of a viscosity modifier for a clear lacquer containing acrylic resin is given below:

- acrylic acid-butyl acrylate-hydroxypropyl methacrylate-methyl methacrylate-styrene polymer;
- microdispersion containing maleic anhydride and a copolymer of hydroxyethyl acrylate and *t*-butyl acrylate;
- toluene diisocyanate (TDI);
- octylamine.

The addition of the viscosity modifier is used to prevent paint from sagging whilst on a vertical surface [19].

With regards to PEX only one example of a polymer viscosity modifier was found in the literature. This may be due to the requirement that the polymer must be soluble in the liquid carrier and that polymers tend to have very high thermal coefficients of viscosity (3 times greater

than fumed silica) [1]. LLNL used polyvinyl fluoride (PVF) and poly(hexano-6-lactone) (PCL) in their RX-52 series which uses TATB as the energetic filler [9]. More details of the RX-52 series are given in Section 3.1.

3 Paste Explosives (PEX)

3.1 TATB

Work by LLNL investigated the inclusion of bimodal TATB into a paste formulation [9]. Currently TATB is available in two particle size distributions; wet-aminated (coarse) with a mean particle size of $36.4\ \mu\text{m}$ and an ultrafine (fine) with a mean particle size of $3.4\ \mu\text{m}$. A series of pastes, labelled RX-52, were produced with a range of solids loading from 40 to 70%. The ratio of coarse/fine TATB was kept constant at 72.5:27.5, respectively. The liquid carrier of the PEX was a specially developed energetic liquid bis(2-fluoro-2,2-dinitroethyl)difluoroformal (FEFO) with a density of $1.607\ \text{gcm}^{-3}$. The viscosity modifiers were two polymers; PVF (1.17–2.34%) and PCL (1.4–2.8%). The molecular weights for the polymers were not reported.

The paste formulations were compared by measuring the steady shear viscosity. For low solids loadings 55–65%, there were very small changes in viscosity as the shear rate increased. Below 55% solids loading settling of the TATB was observed. Above 65% there was a significant increase in viscosity at low shear rates. The results are presented in Figure 2.

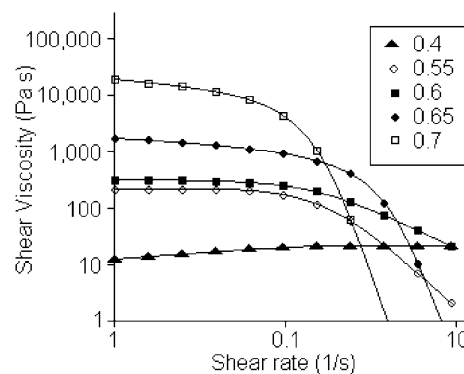


Figure 2. Effect on shear rate on the viscosity for bimodal TATB (27.5:72.5 of Ultra fine/wet aminated) [1].

3.2 HMX

Two studies have been performed using HMX as the explosive filler for PEX. The first is related to the production of an injection mouldable PEX that requires paste like characteristics in order to transfer the composition from the mixing vessel to a container for up to a month after mixing [1]. The ingredients for the PEX are presented in Table 3.

Table 3. Formulations for PEX.

Composition	% w/w	Comments
Injection mouldable PEX		
HMX	73.95	
TMETN	19.33	Energetic fluid
Tone 260	5.04	Polyester polyol
Tone 6000	0.78	Polyester polyol
N-100 polyisocyanate	0.91	Cross-linker
Dabco T-131	0.007	Mercaptotin catalyst
Colloidal PEX		
HMX	72.8	
FM-1	14.8	Energetic liquid content
EDNP	10.3	Energetic modifier for viscosity
Cab-O-Sil	2.0	Colloidal agent, i.e. fumed silica
Ethylene glycol	0.1	Gel enhancement agent
Polymer PEX		
RDX	63	Particle size no greater than 25 μm
Nitrocellulose	6–8	Energetic binder
Tri-butyl acetyl-trate	25–30	Plasticizer
Diphenylamine (DPA)	0.4	Stabiliser

The concept for this formulation was that the uncured system could be transferred as a paste at any time whilst the N-100 polyisocyanate was not present. The study then investigated the effect on viscosity when the size differential between coarse and fine particles was changed. The coarse HMX particles ranged from class 1 (mean particle size = 162 μm) to sieved >43 μm (mean particle size = 90 μm). The fine particles ranged from sieved <43 μm (mean particle size = 9.8 μm) to fluid energy milled (mean particle size = 3 μm). The series of formulations were labelled as RX-08.

Using a Malvern light scattering apparatus it was found that class 5 (mean particle size = 4.0 μm) was actually bimodal, with ~20% of the particles being submicrometer and ~70% between 8 and 12 μm . When the viscosities of the nine formulations were measured, the lowest viscosity was observed in samples which contained 100 μm coarse HMX and class 5 (4.0 μm) fine HMX. As mentioned previously the bimodal nature of the class 5 fine HMX resulted in the formulation being trimodal. It was thought that this contributed to the low viscosity.

The second HMX PEX (RX-08-FK) was of a colloidal paste explosive. The ingredients for the formulation are also presented in Table 3 [1]. The particle size distribution or the modality of the HMX was not quoted in the

paper although Teipel [9] states this composition (RX-08-FK) does not have the 72.5:27.5 coarse to fine particle size ratio which as previously stated appears to be the optimum coarse/fine ratio for minimising excess viscosity in the paste formulation. Small scale sensitivity tests were carried out on this formulation and compared to the results for Comp B, RDX and a composition containing 95.5% HMX and 4.5% estane (LX-14). A summary of the results are presented in Table 4. These results suggest there would be little concern in handling or processing the PEX.

It should be noted that the drop hammer test is not a recognised EMTAP test [20], as per the UK testing procedure, however, the result for RX-08-FK suggests that it is less sensitive to impact when compared to RDX. It is worth noting that the recognised EMTAP test for impact is the Rotter impact test [21], which involves confining the explosive and dropping a 5 kg mass from a known height (cm). A safe to handle response level would have to be greater than the Figure of Insensitiveness (F of I) for RDX which is 80. For PEX it would be prudent to test its response under the liquid impact test because the Rotter mass impactor would result in high shear rates occurring around the brass cap, and the paste's behaviour would more resemble a fluid rather than a solid.

Its response to the Susan test [22], which involves a high velocity, confined, crushing impact test involving 0.4 kg of explosive, the results for RX-08-FK were observed to be less than that for LX-14 [1]. For example, RX-08-FK only started to release energy when the velocity of the projectile exceeded 550 fps (170 m s^{-1}), compared to LX-14 which started to release energy at slower velocities of 50 fps (45 m s^{-1}). The same impact test was also performed on formulations containing different energetic liquid carriers (i.e. FEFO, FM-1 and EDNP). The results showed that liquid carriers have an effect on the response observed by the Susan test with FEFO being more sensitive compared to EDNP. This result could not be quantified because the paper did not give any values for this test.

With regards to the bullet impact test, where a 30-calibre copper-jacket round was used, RX-08-FK did not exhibit any reaction compared to LX-14 which has a vigorous reaction with an overpressure of 27 kPa [1].

In order to study the effect of sedimentation a series of vibration tests were also performed on units filled with PEX containing 7% Cab-O-Sil in the liquid phase (RX-08-FR). The units were subjected to random frequency vibrations up to 6.3 G for 8 h. The units were held at (i)

Table 4. Small scale sensitivity test results.

Test	LX-14 ^{c)}	RX-08-FK	Comp B	RDX
Drop Hammer 50% (cm)	53	120	59	29
DTA ($^{\circ}\text{C}$) ^{a)}	240	240	175	205
CRT (cm^3) ^{b)}	0.08	0.39	0.20	0.10
Spark	Not sensitive			

^{a)} Temperature recorded at the onset of the exotherm. ^{b)} CRT Chemical reactivity test measures the gas evolved ($\text{cm}^3 \text{g}^{-1}$) from the explosive over 22 h at 120 $^{\circ}\text{C}$ (data from von Holtz [1]). ^{c)} 95.5% HMX and 4.5% Estane.

ambient temperature, (ii) 60 °C for 2 h then cooled to ambient temperature and (iii) –50 °C for 24 h then warmed up to ambient temperature. The results of these tests showed that sedimentation only occurred in samples which were initially cooled to –50 °C. Here the upper portion lost a small amount of HMX to settling.

3.3 RDX

There are very few examples in the literature of RDX PEX. Most of the publications are found within patents applications. However, there is information in the literature on RDX based ‘pastes’. The first relates to a formulation that is not strictly a PEX but a paste-like material that can be extruded. As extrusion requires the application of a high shear in order to move the material, then this paste-like material could be considered as a PEX (remembering that it requires high shear) [23]. The ingredients for this paste-like material are presented in Table 3. The high percentage of plasticizer in combination with the nitrocellulose would give the material favourable rheological properties although the viscosity and rheology of the final material was not reported.

The next example of an RDX PEX is a report from the USA which refers to the evaluation of liquid explosives for foxhole digging [24]. The important characteristics of an explosive for foxhole digging are pourability and functionability at –40 °F (–40 °C). Five formulations were evaluated, of which three were based on mixtures of nitromethane, nitroethane and RDX, with viscosities varying from liquids to pastes. The formulations are presented in Table 5. It is interesting to note that nitromethane has a freezing point of –34 °C. This freezing point can be lowered by adding nitroethane which has a freezing point of –68 °C, for example a ratio of 75:25 of nitromethane/nitroethane results in a freezing point of –40 °C. The report described the percentage (w/w) of each component required to create a liquid, slurry and paste.

The results presented in Table 5 suggest that a reduction in the liquid carrier phase and an increase in the suspended particles result in an increase in viscosity. Concomitantly the compositions change from a liquid to a paste as the viscosity increases. It is interesting to note that the use of Cab-O-Sil was not used in the paste formulation; this is probably due to nitrocellulose acting as a polymeric gelling agent. The actual viscosities of each system were not reported, however, for the purpose of foxhole digging the paste formulation was not considered suitable as it did not ‘flow well’ into the ground.

Table 5. Examples of liquid explosive compositions for foxhole digging [24].

Liquid	Slurry	Paste
59.9% nitromethane/nitroethane	48% nitromethane/nitroethane	24% nitromethane/nitroethane
30% RDX class E ^{a)}	30% RDX class E	15% RDX class E ^{a)}
10% aluminium	20% aluminium	60% RDX class A ^{a)}
0.5% Cab-O-Sil M-5 ^{b)}	2% nitrocellulose	1% nitrocellulose

^{a)} Class E and A are an old classification for RDX particle size from MIL-R-398C specification. ^{b)} Cab-O-Sil is a synthetic, amorphous, untreated fumed silicon dioxide.

The other two formulations which were evaluated for foxhole digging were (i) a two part gelled slurry mix and (ii) a two part liquid formulation. The former was a binary mixture of NaClO₄ in solution and an aluminised dry fuel. The latter consisted of 70% hydrazine and 15% water as the liquid phase, and 80% ammonium nitrate with 20% ammonium perchlorate as the solid phase. The two parts were mixed in a 2:1, solid/liquid ratio.

A patent by Titan Artifices in France [25] refers to pastes which contain nitroalkanes (nitromethane to nitrobutane) with a thickening agent. The composition containing 70% w/w nitromethane, 24% w/w nitroethane and 6% w/w pyrogenic SiO₂ results in a fluid which is stable between –40 to +70 °C and insensitive to a No. 8 detonator. The patent suggests that nitrocellulose or a solid explosive (i.e. RDX) may be included in the formulation as well as antigelling, reinforcing and/or sensitising agents. The patent did not contain any data on the rheology and viscosity of the compositions.

Details of an improvised RDX PEX have also been reported on a website [26]. The author describes the mixing of Comp 4 with mineral oil to create a paste. The formulation for this composition is presented in Table 6.

This formulation results in a mouldable composition. The properties of this composition can be changed to produce a paste-like material by adding 0.2 L of mineral oil to 0.57 kg of Comp 4. Details of the paste-like formulation are also presented in Table 6. By introducing more oil the percentage of RDX is reduced to match the criteria described earlier for PEX. Secondly, if the RDX was bimodal, then this would increase its paste-like characteristics. Also the percentage of fluid is ideal; the only disadvantage is the density of the oil and its lack of energetic content, which would affect the overall performance.

Table 6. Details of improvised RDX PEX [26].

Mouldable Composition	Paste-like Composition
91% RDX	69% RDX
5.3% dioctylsebacate (DOS)	4% dioctylsebacate (DOS)
2.1% polyisobutylene	1.6% polyisobutylene
1.6% oil	25.4% oil

4 Other Systems

Very few other articles appear in the open literature that relate specifically to the production of energetic pastes. Some of the reports and literature already discussed de-

scribe the use of energetic liquids, in combination with a gellating agent in order to create a paste [26]. Other papers describe the use of energetic salts in conjunction with fuels to create paste-like materials [13–15,24].

One further example, from a US patent, reports the use of CL-20 and other nitramines to create pastes as a replacement for Comp 4 [27]. The patent proposes two concepts for creating a more mouldable explosive composition for field work. The first concept describes the addition of additives to Comp 4 to create a paste, and the second concept describes a paste which contains CL-20 and HMX suspended in a high viscosity silicone fluid (polydimethylsilicone fluid). Details of the compositions are presented in Table 7.

Table 7. Details of a PEX containing CL-20 [27].

Composition A	Composition B
16.17 % CL-20	26.0 % CL-20
60.97 % RDX	45.5 % RDX
16.83 % BDNPA/F	21.5 % BDNPA/F
3.55 % Dioctylsebacate (DOS)	2.65 % Dioctylsebacate (DOS)
41 % Polyisobutylene	1.50 % Polymethylphenylsiloxane (PMPS)
	1.05 % Polyisobutylene
1.07 % Fuel oil	1.00 % Cellulose acetate butyrate (CAB)
	0.8 % Fuel oil

From Table 7 it can be seen that for composition A the total nitramine content is 77.14% with just over 18% for the liquid content. For composition B the total nitramine content is less than composition A (71.5%) but it contains a greater percentage of liquid carrier (~25%). The particle size for CL-20 was not reported in this patent, but in other papers and patents the particle size was reported to be 2 μm . The patent also contained calculated values for the theoretical maximum densities (TMD), P_{CJ} (C–J Pressure) and velocity of detonation (VoD). Both compositions compare favourably to the values reported for Comp 4 (i.e. TMD = 1.64 g cm^{-3} , P_{CJ} = 24.6 GPa and VoD = 7800 m s^{-1}).

The patent also reported on other PEX compositions containing CL-20, HMX and a silicone fluid. The details are given below:

- 70 % CL-20 (2 μm);
- 10 % HMX (2 μm);
- 20 % polydimethylsilicone fluid (5000 mPas).

Table 8. Calculated performance properties for selected PEX formulations.

Calculated Performance (% , w/w)	Comp 4	Comp 4 Paste	Foxhole Liquid	Foxhole Slurry	Foxhole Paste	RX-08-FK	HMX [28]
TMD (99%) (g cm^{-3})	1.64	1.32	1.34	1.45	1.56	1.749	1.89
P_{CJ} (GPa)	24.6	13.5	16.6	16.4	24.9	31.3	39.2
VoD (km s^{-1})	7.80	6.41	6.52	6.38	7.63	8.14	9.11
Temperature (K)	3836	3284	3800	4337	3548	–	–
Total energy (kJ cm^{-3})	8.79	7.00	7.71	10.20	8.26	–	–

The softening point of this paste was recorded at -38°C ; no other data was reported in the patent.

5 Performance

As well as having ideal physical properties the PEX should function as an energetic material. Calculated performance data for selected PEX formulations are presented in Table 8 together with data for Comp 4 and HMX.

From Table 8 it can be seen that the paste Comp 4 is an example of a composition which is not designed for a specific performance output. The addition of fuel oil to produce a paste has reduced the TMD and VoD by ~20% and the P_{CJ} by 45% when compared to Comp 4.

When the results for paste Comp 4 are compared to the paste formulation for Foxhole digging, the calculated performance for the latter can be seen to be improved (see Table 8). Here the performance is closer to the performance expected for Comp 4. This is mainly due to the use of energetic liquids (nitroethane/nitromethane) as the liquid carrier.

It can also be seen from Table 8 that the overall performance of a paste can be significantly improved when the density of the energetic liquid is similar to that of the crystalline material. This can be observed in paste RX-08-FK which contains 74.5% HMX and 22.9% energetic liquid. Here the values of the densities for both materials lie between 1.5 and 1.6 g cm^{-3} resulting in a reduction of the TMD of the paste by 8%. A reduction in the VoD and P_{CJ} by 11 and 20%, respectively can also be observed when compared to HMX.

6 Future Explosive Pastes (PEX) and Smart Paste Explosives (SPEX)

The published literature on PEX is very limited. This may be due to researchers not publishing their work or very little research has been carried out in this area. However, with the push for Insensitive Munitions (IM) and the increase environmental awareness, the future of PEX is very bright. Future PEX will no doubt contain energetic materials which are suitable for IM such as FOX-7, FOX-12, HNS and TATB together with a suitable liquid resulting in the optimum rheological properties. It may be worth considering oligomers and polymers of energetic polyphosphazene which have high densities for the polymers i.e. 1.45 to 1.69 g cm^{-3} [29,30]. These high

densities are a closer match to most explosives compared to the polymeric forms of polyNIMMO and polyGLYN which have densities of 1.25 and 1.4 g cm⁻³, respectively [29]. Energetic polyphosphazenes can be synthesised with a range of energetic side chains, from 0 to 100%, resulting in a polymer with a tuneable energy density [31]. The addition of the side chains could also be used to tune the physical properties of the liquid polymer to the properties of the energetic filler and hence the overall rheological properties of the paste.

Another approach would be to formulate SPEX and could be incorporated into future weapons designs for IM-compliant munitions. The SPEX would be capable of flowing like a liquid and when an external stimulus is applied, i.e. magnetic, electrical, light, etc., the SPEX would become a solid. This process would be instantaneous and reversible. In the paste form the material will be less energetic and therefore provide a method of desensitisation which would be an advantage during storage, transportation and demilitarisation.

A method of producing SPEX is to use the technology of magneto (MR) and electro (ER) rheological fluids. These fluids are capable of changing their physical parameters when either a magnetic or electrical field is applied. ER fluids are typically suspensions of semiconducting, solid particles dispersed in an insulating carrier liquid. In order to make an MR fluid the electric polarization (for ER fluids) is replaced by a magnetic polarization [32]. These fluids require a material to be suspended in another material, e.g. strontium titanate particles dispersed in silicone oil [33]. Of the particles suspended in the fluid, a fraction must be polarisable when the external field is applied (for ER fluids). Also the fluid must be insulating otherwise the charge would dissipate. The major consideration for both of these fluids is that the densities of dispersed phase and the dispersant should be similar to prevent sedimentation. Of the papers reviewed in Akhavan's paper [32], the fraction of particles suspended in the fluid was up to a maximum of 40%. This is some way short of the 65% required for a PEX. It would also be expected that most liquids quoted in this report would not be good insulators.

Recent work at Cranfield University has been in the development of energetic mesogens based on azoxybenzene compounds [34]. It is intended to link these energetic mesogens to a polymeric liquid crystal material, where on the application of an external stimulus the mesogens will change to a different liquid crystalline state. The proposed programme of work is to (i) synthesis polymers with functional side groups and their 5-aminotetrazole energetic salts, (ii) synthesis copolymers with functional side groups and their 5-aminotetrazole energetic salts and (iii) grafting of these polymers and copolymers using side groups to impart liquid-crystalline properties to their energetic salts.

7 Conclusion

From this literature review it is evident that in order to create a PEX there are criteria to which one must adhere. This entails not just the creation of a PEX but one that will give the desired performance, undergo transfer when a sufficient force is applied, and yet not separate into its component parts whilst being stored.

Several papers and patents discussed the formation of pastes yet did not cover the rheology of the material either during or after manufacture. This aspect was missing from most of the early papers, but has been addressed more recently by von Holtz [1] and Teipel [9]. Understanding the rheological properties of the paste is crucial for inclusion in a weapon systems whereby the material is transferred from one location to another. Work by the French has begun to investigate the effect of wall shear on pastes as they are moved [35]. LLNL have also determined the shear stress for their RX-08 series using a capillary rheometer, and created a processing method and loader for filling of devices with pastes [1].

Currently there appears to be two clear lines for the production of pastes:

- take a current formulation, that is not cross-linked, and add the necessary additives to create a paste-like system, or
- start from a base explosive and create a paste with an energetic carrier and a gelling agent.

The latter method will take a greater period of time, yet the knowledge obtained during that process would be greater than the former method. Issue of component compatibility will be automatically raised when using the 'additive' process and this could prove costly in the long term if all the ingredients are not known.

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