Enhanced Energetic Polyphosphazenes

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Energetic polymers can assist in the formulation of low hazard, high power explosives by facilitating reduced solids loadings without loss of power. However, the difficulty is to obtain viable polymers with adequate energy-density. We have previously described a unique range of energetic binders based upon the polyphosphazene backbone, specifically developed for application to energetic systems[1]. These mixed substituent polyphosphazenes have been shown capable of combining high energy-density with favourable physical and hazard properties. We report here on their potential, when used in admixture with polyNIMMO or polyGLYN to enhance energy-density, and depress glass transition temperature. We also describe the preparation of novel homopolymer variants by a different synthetic route. In these materials energy has been maximised by fully substituting the polyphosphazene backbone with energetic moieties. Thus nitrato substituted products have been prepared with measured energy densities up to 63% above that of polyGLYN. Interestingly, the properties of homopolymer azides prepared using the new route have been found to differ significantly from earlier mixed substituent analogues. Thus, the new materials are largely tractable and possess low glass transition temperatures, down to almost minus 100°C. This paper details characterisation data for these new energetic polyphosphazenes. Compatibility and small-scale hazard test data are also reported in relation to the preliminary formulation of selected mixed substituent polyphosphazenes with HNS, HMX, TATB and FOX-7.

Solids loading is a key feature in determining the hazard characteristics of many high performance plastic bonded explosive (PBX) formulations. Energetic polymers can be valuable tools for reducing the solids loadings of PBXs, without excessive loss of energy. However, the difficulty is to obtain viable energetic polymers possessing adequate energy-density and also, preferably, low glass transition temperatures (T_gs).
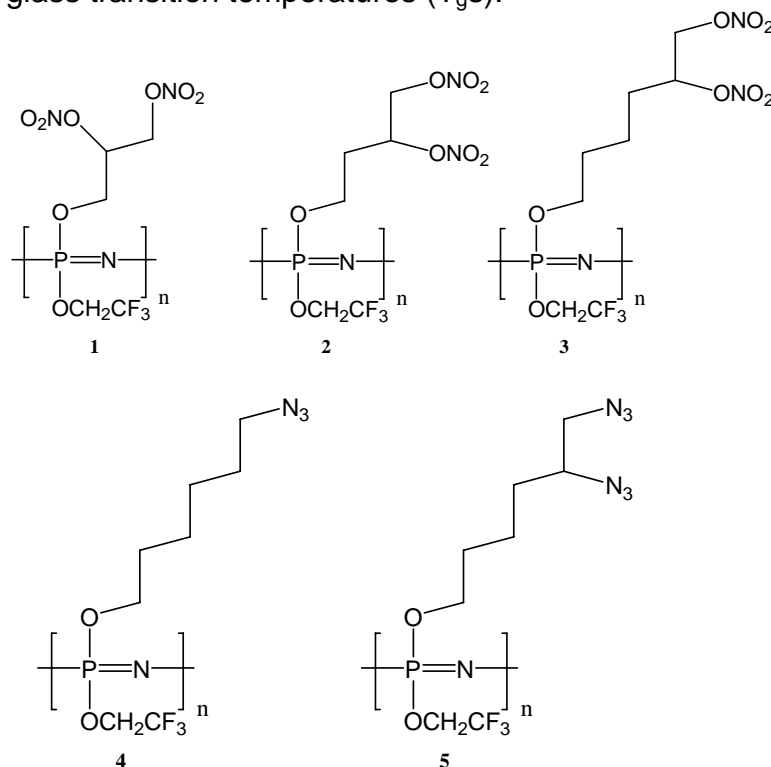

Figure 1: Synthesised energetic polyphosphazenes (Simplified structure[1]) Ratio of energetic:trifluoroethoxy (TFE) side groups can be varied.

We have previously described[1] a unique range of mixed substituent energetic polyphosphazenes (Figure 1), which combine high energy-density with favourable physical and hazard properties. Whilst some of these materials have been shown to be effective binders using a solvent paste process (see on) they are not chemically curable. As it is advantageous to be able to cure the binder system for some applications, particularly those requiring low solids loadings, we are exploring the synthesis of curable energetic polyphosphazenes. Pending completion of this work we have examined curable mixed polymer systems based upon the previously reported energetic polyphosphazenes in admixture with polyNIMMO [poly(3-methyl-3-nitratomethyl oxetane)] or polyGLYN [polyglycidyl nitrate]. The resultant binder systems may be cured using standard isocyanate technology, due to the presence of polyNIMMO or polyGLYN, but promise higher energy-densities than the pure carbon based materials.

Blends of polyphosphazene **3** (70% nitrate ester, 30% TFE) and polyGLYN have been found to be homogeneous, each initially demonstrating a single T_g. Table 1 records T_g and energy-density data for various binder ratios, from which it may be observed that the T_g of uncured polyGLYN is depressed by the addition of the polyphosphazene.

Weight fraction of PolyGLYN	Weight fraction of **3**	T_g (°C) (Uncured)	Energy density $(J/cm^3)^*$
100	0	-31.1	2900
75	25	-32.4	3117
60	40	-32.7	3247
50	50	-37.3	3334
40	60	-40.3	3421
25	75	-43.3	3551
0	100	-45.8	3768

* Data interpolated from density and decomposition energy (DSC) values for pure materials

Table 1: Data for PolyGLYN/polyphosphazene **3** mixed binders

For each mixture the T_g falls between the values of the individual components, as illustrated graphically in Figure 2. However, the observed transitions deviate somewhat from a simple linear relationship, based on the weight fractions of the individual components (the dotted line); such deviations are common with polymer blends (due to interactions - such as hydrogen bonding - between the two polymers). Blends of the same polyphosphazene **3** with polyNIMMO also yielded apparently homogeneous mixed binder systems, but in this case each blend demonstrated two separate T_gs (Table 2). However, repeat experiments with different batches of polymer showed that blends of **3** with either polyGLYN or polyNIMMO could variously
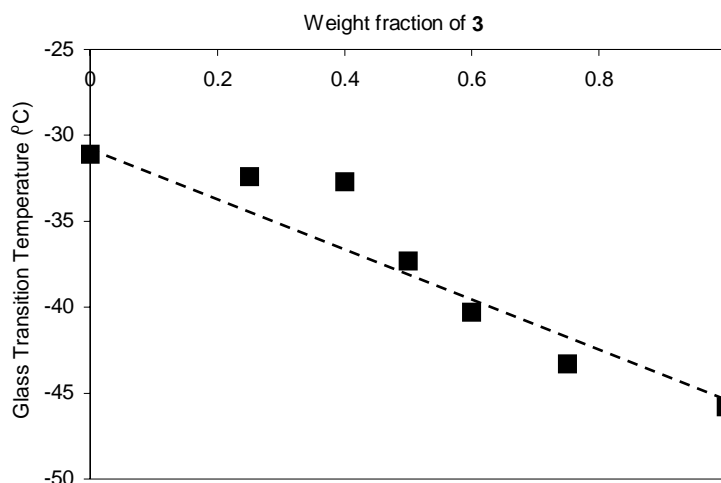
Figure 2 Variation of T_g with weight fraction of ingredients in a mixed binder containing polyGLYN/polyphosphazene **3**

yield twin T_gs comparable to those of the parent polymers or single T_gs between those of the two components. Most likely, these conflicting data reflect experimental variations, perhaps in sample preparation technique (eg thermal history) or differences in oligomer or other small molecule content between different batches of polymer. Further work will be required to clarify the position. However, the potential for polyphosphazenes to depress the T_g of either polyNIMMO or polyGLYN is worth exploring, because significant loss (exudation) of the polyphosphazene through life is unlikely from this type of mixture, due to its relatively high molecular weight (>10,000 Da), low volatility and the chemical similarity of the pendent side chains in the two materials.

| Weight fraction of PolyNIMMO	Weight fraction of **3**	T_g (°C) (Uncured)	Energy density (J/cm^3)*
100	0	-32.8	1638
80	20	-28.7, -43.4	2064
60	40	-29.6, -44.3	2490
40	60	-30.4, -46.0	2916
0	100	-45.8	3768

* Interpolated from measured densities and decomposition energies (DSC) for pure materials

**Table 2** Data for polyNIMMO/polyphosphazene **3** mixed binders

The above mixed binder systems containing polyphosphazene **3** and polyGLYN or polyNIMMO have been prepared and cured in both 50:50 and 60:40 ratios (IPDI/dibutyltindilaurate, 60°C, 1.1 molar equivalent with respect to the hydroxyl functionality of polyNIMMO or polyGLYN). The products were soft, high tack, extensible rubbers. However, as the mixed binder based upon polyGLYN was deemed to be significantly under cured using these conditions,

further optimisation of the isocyanate content/cure conditions is believed to be necessary for this formulation.

The energetic polyphosphazenes previously described have been prepared using nucleophilic substitution of poly[bis(trifluoroethoxy)phosphazene][1] with various alkoxides. Whilst this approach is effective in producing products with a wide variety of substitution patterns, it has proven unsuitable for the preparation of products containing more than around 70% energetic side chain substituents. This limitation has placed restrictions on the maximum energy content of the final polymer. We now report an alternative synthesis which permits unrestricted substitution by the energetic moiety and hence the formation of 100% energetically substituted polyphosphazene homopolymers, which offer maximised energy contents.
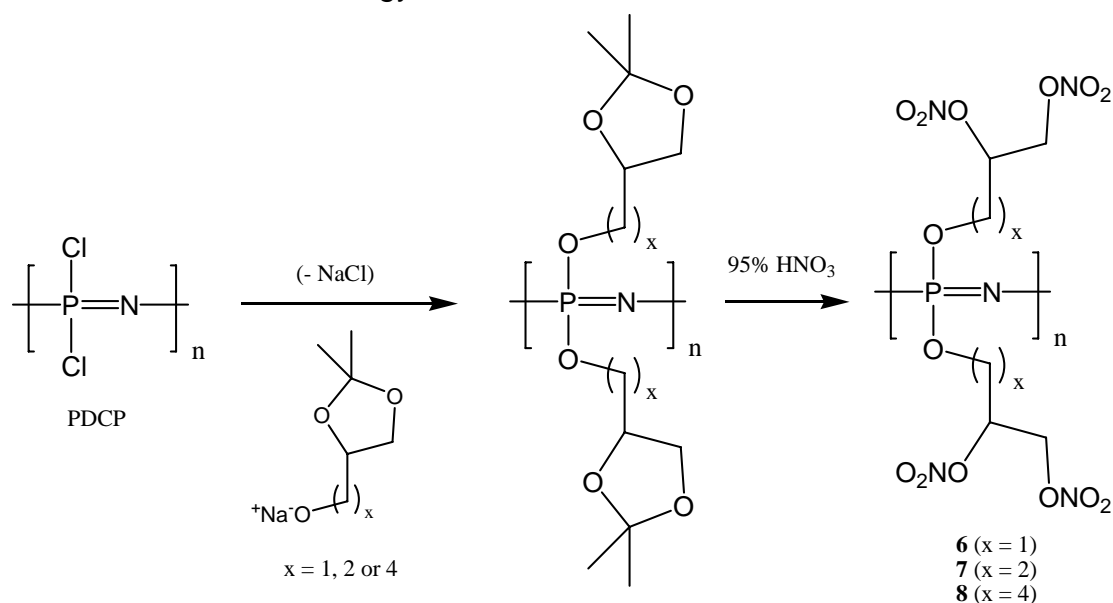
Scheme 1a Synthesis of polyphosphazenes **6,7** and **8**
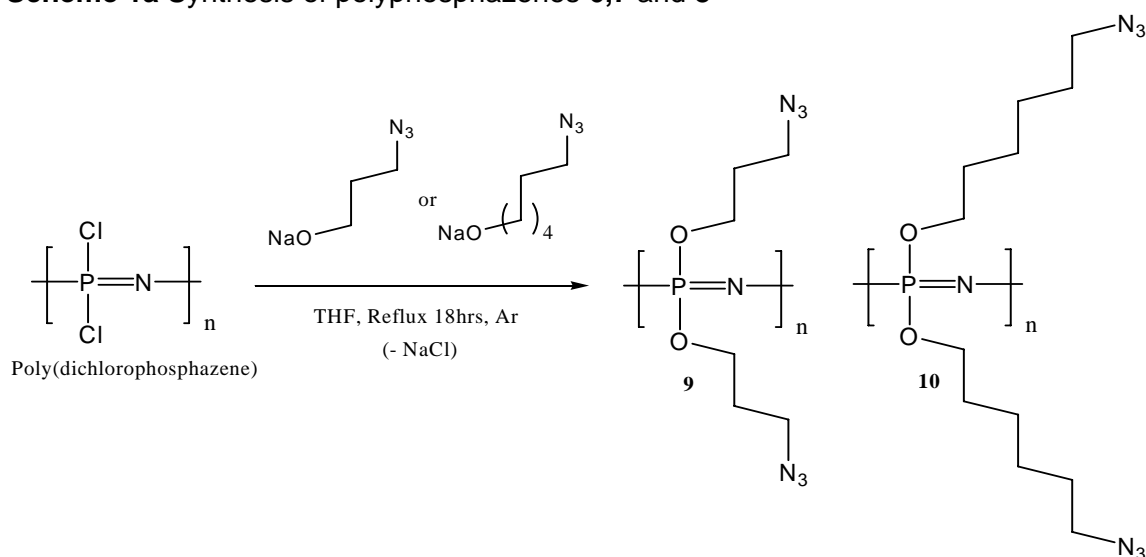
Scheme 1b Synthesis of polyphosphazenes **9** and **10**

The new route (Scheme 1) involves synthesis of polydichlorophosphazene[2] and subsequent reaction of this with the sodium salt of an alcohol. Not only is it possible to achieve any desired degree of substitution using this procedure, simply by controlling molar ratios, but also it is possible to prepare mixed substituent products through the reaction of multiple alcohols. For those products containing nitrate ester groups (**6-8**) a final nitration step is also required.

In the case of nitrate ester substituted polyphosphazenes the main advantage of the new route is the preparation of 100% substituted products possessing enhanced energy. Thus, the homopolymers **6,7** and **8** have now been prepared, which demonstrate energy-densities up to 63% above that of polyGLYN (Table 3). Characterisation data for these materials is also presented in Figure 3, together with that for the previously reported mixed substituent products **1-3**, to illustrate trends in physical properties. In the case of azide substituted materials the utility of the previous synthetic route has been somewhat limited, as products of the type **4** and **5** containing more than about 40-50% energetic side groups have become intractable[1]. In contrast the route illustrated in Scheme 1 has permitted the synthesis of well defined, soluble polymers with up to 100% energetic side chain substitution. The polyphosphazene homopolymers **9** and **10** comprise two such materials, which both exhibit particularly low T_gs. For example **10** has a T_g of -99^oC. Whilst the energy-density of these azides is below that of polyGLYN, **9** still shows a 50% increase in energy-density relative to polyNIMMO and couples this with a much lower T_g (-73^oC). Consequently, these materials may be of value to applications for which a low T_g is more significant than a particularly high energy-density. Product data is presented in Table 3.

Polymer	Decomposition Energy (DSC) $(J\ g^{-1})$	Density $(g\ cm^{-3})$	Energy Density $(J\ cm^{-3})$ [% higher than PolyGLYN]	Glass Transition Temperature $(^{\circ}C)$
6	2690	1.69	4550 [57]	-32.5
7	2880	1.65	4750 [63]	-23.8
8	2760	1.45	4002 [38]	-35.2
9	1825	1.35	2465	-73
10	1665	1.16	1930	-99
Mixed Substituent Polyphosphazenes[1]	2020 – 2430	1.52 – 1.65	3333 – 3792	-13 to –55
PolyNIMMO	1300	1.26	1638	-33.0
PolyGLYN	2000	1.45	2900	-30.0

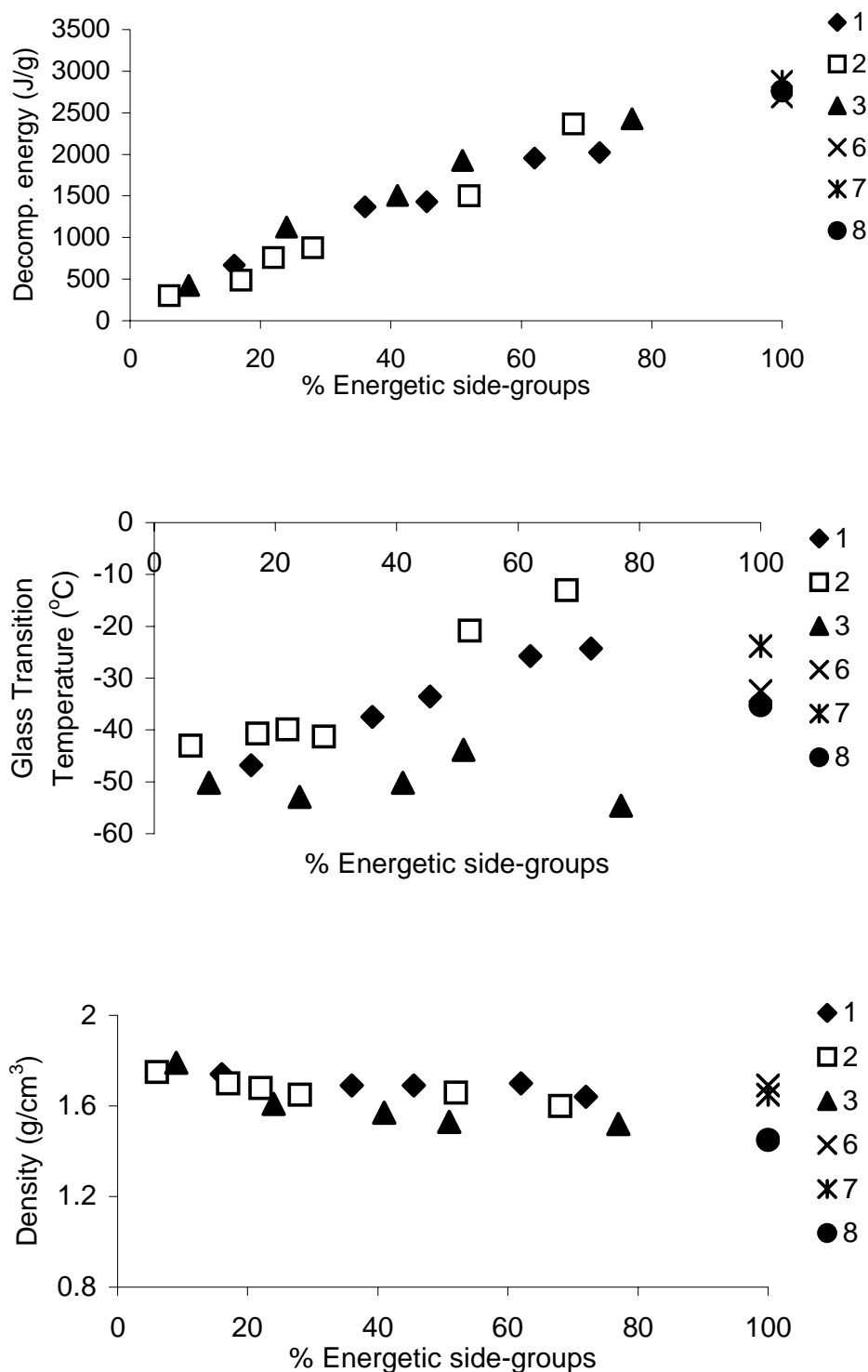**Table 3** Properties of Energetic Polyphosphazene Homopolymers in comparison to polyNIMMO and polyGLYN

Figure 3: Graphs illustrating trends in (i) decomposition energy, (ii) T_g and (iii) density, for nitrato substituted polyphosphazenes **1**, **2**, **3**, **6**, **7** and **8**

Preliminary formulation has been undertaken on selected mixed substituent polyphosphazenes with the high explosives (HE) HMX, TATB, FOX-7 and HNS. A solvent paste process (THF) was employed which after drying (40°C, 30min), yielded free flowing, but cohesive moulding powders. These powders

readily produced robust pellets using a double-ended die press (cylindrical, 11.4mm diameter, 2 ton, 5 minutes). Densities of up to 95.4% of TMD were obtained without the application of vacuum (Table 4). Generally the pellets were well defined, but sometimes at higher binder loadings damage resulted from adhesion of the material to the die. This feature is shown in Figure 4, which illustrates some typical examples of moulding powders and pressed pellets. The present work was performed on a small-scale using hand mixing for the purpose of preliminary screening, it is believed that higher pressing densities will be achievable through the use of more sophisticated equipment.

Small-scale hazard test/compatibility results and pressing densities for the moulding powders are given in Table 4. Generally these are regarded as satisfactory with the exception of HNS/**3**, at 10% binder loading, which produced a particularly low F of I and an increased number of fires on the small-scale mallet impact test (steel on steel). The reason for this is not fully understood. The colour change observed with HMX/**4**, together with the depressed temperature for onset of decomposition, also require further investigation as these may reflect chemical incompatibility. [The recorded 'Langlie F of I' data represent an abridged Figure of Insensitiveness testing regime.] When considering the data in Table 4, it should be noted that energetic polymers which contain thermally labile groups (such as nitrate ester) would be expected to decompose to some extent during the F of I test, simply due to thermal effects. We believe that this accounts for the reduction in F of I observed with some high explosives. Thus, there is a steady reduction in F of I for several TATB and HNS formulations, as the percentage of a specific nitrate ester binder is increased (Table 4). [At present we have no evidence of chemical incompatibility between these ingredients.] A similar effect has been noted with another nitrate ester formulation based on commercial polyGLYN. Thus the F of I observed for a polyGLYN/FOX-7 composition was found, unexpectedly, to be lower than those of its ingredients. Nevertheless, the formulation did not show sensitivity to a detonation shock wave.[3] To date, whenever evolved gas volumes have been measured during the F of I testing of energetic polyphosphazenes, either alone or in admixture with high explosives, they have been found to be low. On this basis we currently believe that these polyphosphazene binders are of low explosiveness.

Conclusions

Recent work has expanded the available range of energetic polyphosphazenes yielding products with the highest measured energy-density and lowest recorded glass transition temperature within the current product set. Highly azide substituted polyphosphazenes prepared via the polydichlorophosphazene route demonstrate significantly different properties to materials previously synthesised via poly[bis(trifluoroethoxy)phosphazene]. Thus they are soluble, tractable materials and it is the 100% azidated product **10** which demonstrates the lowest T_g obtained to date. The glass transition temperatures observed with these materials are noteworthy because they are dramatically lower than those available with any other classes of energetic binder – without plasticization. Furthermore, the flexibility of the

polydichlorophosphazene synthetic route may assist optimisation of mixed substituent products, so as to combine a range of particularly desirable properties within a single polymer.

The feasibility of creating curable mixed binder systems containing polyphosphazenes in admixture with either polyNIMMO or polyGLYN has been demonstrated. Such systems have the potential for enhanced energy-density relative to the pure carbon based systems and possibly also of reduced glass transition temperatures.

The polyphosphazenes tested to date exhibit good binder properties when formulated with HMX, TATB, FOX-7 and HNS. Generally they produce free flowing but cohesive moulding powders, with acceptable small-scale hazard properties. We find these preliminary results encouraging. Further formulation and testing of these materials is in progress and will be the subject of further communications.

References

1. P. Golding and S. J. Trussell, Energetic polyphosphazenes – a new category of binders for energetic formulations. Paper presented at 2004, NDIA Insensitive Munitions and Energetic Materials Technology Symposium, November 15-17, 2004, Hilton Hotel, San Francisco, CA.
2. i) Polymerisation: H.R. Allcock, C.A.Crane, C.T Morrissey, J. M.Nelson, S.D.Reeves, C.H.Honeyman, I.Manners; Macromolecules 1996,29,7740; ii) Monomer synthesis: B.Wang, E.Rivard, I.Manners; Inorg.Chem.2002,41,1690.
3. C.Eldsäter, H.Edvinsson, M. Johansson, Å.Pettersson and C.Sandberg, Formulation of PBX's based on 1,1-diamino-2,2-dinitroethylene (FOX-7), 33rd International Conference of ICT, June 25-28, 2002, Karlsruhe, FRG.

Table 4: Hazard Test Results and Pressing Densities for Explosive Compositions with Energetic Polyphosphazene Binder

| HE	Polyphosphazene type	Percentage of energetic side group substitution	% Binder	Colour Change at 100°C	Onset of decomposition (DSC) ^{o}C	Small-Scale Mallet Impact Steel/Steel Direct Blow	Small-Scale Mallet Friction Steel/Steel Glancing Blow	Mallet Friction Boxwood/ Yorkstone	Langlie Fof I	Pressed pellet Density (% TMD)
HMX	**3**	70	5	None	279	0/10	0/10	0/50	57.7	93.1
HMX	**3**	70	10	None	277	1/10	3/10			
HMX	**1**	68	10	None	277	1/10	1/10	0/50	61.3	95.3
HMX	**3**	17	10	None	278	1/10	0/10	0/50	72.1	93.7
HMX	**1**	18	10	None		0/10	0/10	0/50	64.0	92.9
HMX	**4**	60	10	Yes	233	2/10	1/10			
TATB	**3**	70	5	None	370	0/10	0/10	0/50	88.1	91.8
TATB	**3**	70	10	None	370	0/10	0/10	0/50	72.6	94.9
TATB	**1**	68	10	None	369	0/10	0/10			
TATB	**1**	68	5	None		0/10	0/10	0/50	64.0	92.9
TATB	**3**	17	10	None		0/10	0/10	0/50	73.9	92.9
TATB	**3**	17	5	None	373	0/10	0/10	0/50	138.9	91.7
TATB	**1**	18	10	None	371	0/10	0/10			
TATB	**4**	60	10	None	360	0/10	0/10			
TATB	**4**	60	5	None		0/10	0/10	0/50	83.9	92.1
HNS	**3**	70	5	None	317	0/10	0/10		50.8	93.9
HNS	**3**	70	10	None	317	3/10	0/10	0/50	18.7	
HNS	**3**	70	1	None		0/10	0/10	0/50	77.6	92.4
HNS	**1**	68	5	None		0/10	0/10	0/50	55.3	90.0
HNS	**1**	68	5							93.8
HNS	**1**	68	1	None		0/10	0/10	0/50	67.1	93.6
HNS	**3**	17	5	None	318	0/10	0/10	0/50	73.9	93.5
HNS	**3**	17	1	None	319	0/10	0/10	0/50	106.0	91.4
HNS	**4**	60	5	None	320	0/10	0/10	0/50	67.1	95.4
FOX7	**3**	70	5	None		0/10	0/10			
FOX7	**3**	70	10	None	269	0/10	0/10	0/50	73.9	91.1
FOX7	**4**	60	10	None	263	0/10	0/10	0/50	80.0	87.9

Figure 4 Photographs of pressed pellets and moulding powder (left) and Scanning Electron Micrographs (right) of some typical polyphosphazene based HE formulations
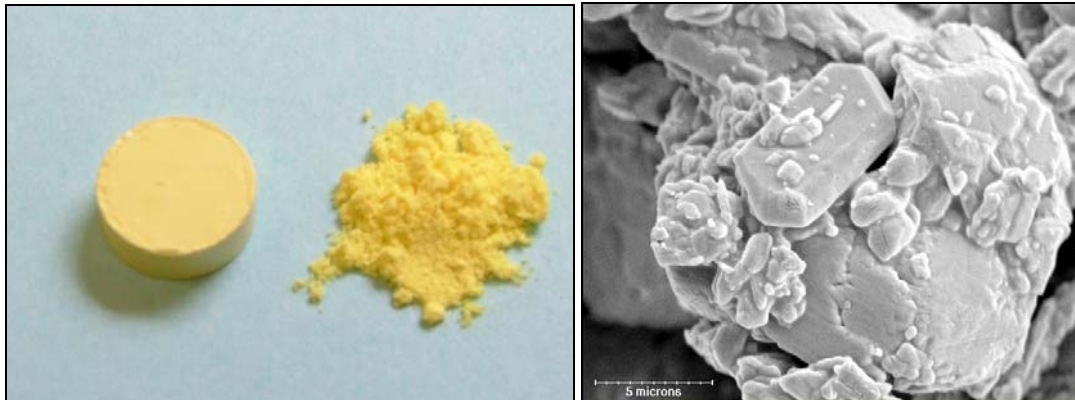
TATB/**3** (70% Nitrate Ester), 95:5 weight percent
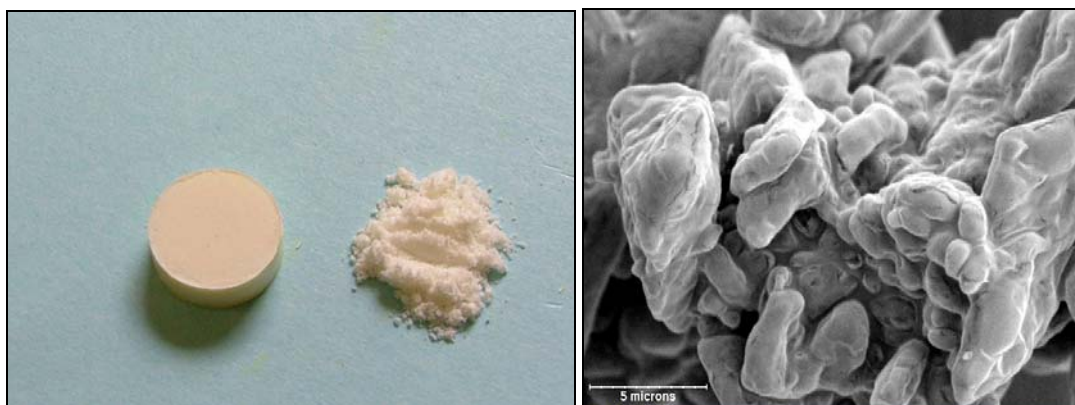
HMX/**3** (70% Nitrate Ester), 95:5 weight percent
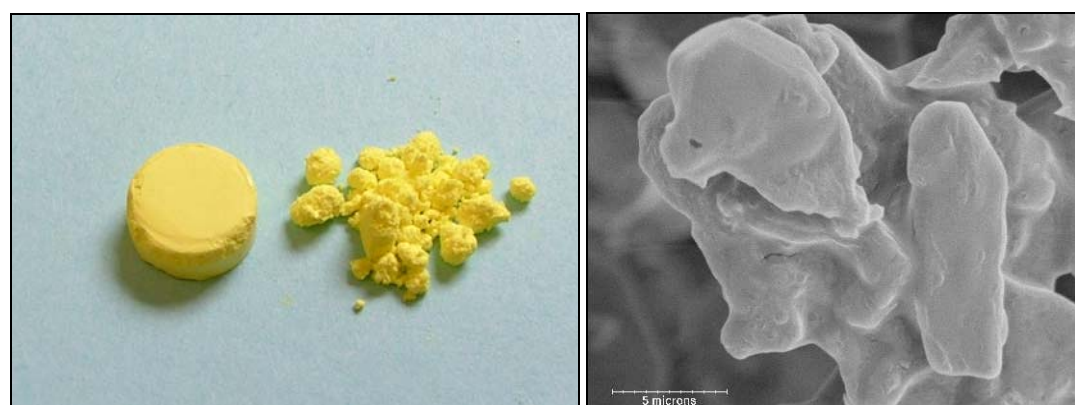
FOX-7/**4** (60% Azide), 90:10 weight percent, showing damage due to mould adhesion