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(54) **Titre :** DESENSIBILISATION DE MATIERES ENERGETIQUES
(54) **Title:** DESENSITISATION OF ENERGETIC MATERIALS

(57) **Abrégé/Abstract:**

An energetic material comprises an energetic crystalline material substantially coated in an energetic plasticiser material. Advantageously the energetic material comprises from 90 to 99% by weight of an energetic crystalline material and from 1 to 10% by weight of an energetic plasticiser material comprising a plasticiser selected from the group comprising Butane Triol trinitrate (BTTN), Trimethylanol ethane trinitrate (TMETN), Diazidonitrazapentane (DANPE), Glycidyl Azide Polymer (Azide Derivative) (GAP Azide), Bis(2,2-dinitropropyl)acetal / bis(2,2-dinitropropyl)formal (BDNPA/F) or mixtures of two or more of these plasticisers. The inventors have found that the combination of just a small quantity of energetic plasticiser material to the energetic crystalline material prior to incorporation into the bulk plasticiser, binder and filler mixture of an explosive or propellant composition has unexpected and advantageous effects.

DESENSITISATION OF ENERGETIC MATERIALS

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DESENSITISATION OF ENERGETIC MATERIALS

This invention relates to the desensitisation of energetic crystalline materials, in particular hexanitrohexaazaisowurtizane (HNIW) (also designated CL20) but also other nitramine explosives such as cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX).

HNIW comprises a high density caged molecule recognised as a suitable energetic filler for propellant materials and explosives. Its use as a potential replacement for
existing fillers such as RDX and HMX in cast double base, composite and novel propellants and other explosive materials has been postulated.

Propellant compositions used for launching relatively high mass projectiles are desirably highly energetic and energetically dense i.e. a small volume of the material will produce high potential kinetic energy via rapid gasification on ignition. In general, such a propellant composition comprises three component materials; an energetic filler, a plasticiser and a binder, the latter two components primarily provide the desirable mechanical properties of the resultant propellant material. Choice of plasticiser and binder for a particular energetic filler will depend on a number of factors such as the projection range for the projectile, the extremes of temperature under which the end product is expected to operate and the chemical and physical interactions of the materials.

However, aside from the functional performance of the propellant material as an end product, industrial manufacturers of novel materials must consider the safety issues associated with the incorporation and manufacture of these filler, binder or plasticiser materials into rocketry. Thus, whilst from a performance point of view an energetic material may appear desirable for use as either a binder, plasticiser or filler in the predicted propellant formulation, the material must be safe for incorporation, processing and transportation. If an unsafe energetic material was to be incorporated into a propellant or explosive system, the unsafe material might initiate during either the manufacturing process or during transportation of the end product. This initiation might be via accidental friction or impact stimulation leading to deflagration or possibly a deflagration to detonation transition within the explosive material sufficient to cause an unwanted premature explosion. For this reason of safety, most known propellant materials (e.g. Ammonium Perchlorate / hydroxy terminated polybutadiene based composite propellant) comprise, comparatively, energetically inert plasticiser and binder components.

In general, solid propellant materials such as those based on Ammonium Perchlorate, Hydroxy terminated polybutadiene (binder) and dioctyl sebacate (plasticiser) are manufactured by a dry mixing and blending process : this means that no additional desensitising solvent s (e.g. water) are added to this mix other than those that will be incorporated into the final propellant formulation. This dry mix, once manufactured, is treated to facilitate curing of the binder material to provide the desirable mechanical properties for the propellant material. This method is generally considered preferable to a wet mixing process (where additional solvent is included as transport media or processing aid or as a desensitiser to improve safety) as it provides better homogeneity of mixing, and minimises delays in cleaning mixing equipment or drying out of the mixed end product prior to further processing (e.g. casting and curing).

Typically, existing propellant materials comprise around 6% by weight plasticiser to 85% by weight energetic filler. The propellant material will also generally comprise around 9% by total weight of binder and other filler materials.

HNIW is a highly friction sensitive material having a rotary friction test Figure of Friction (F of F) of 0.7 and produces a highly ferocious response on reaction via friction stimuli. The exceptionally low F of F of HNIW (when compared against other ingredients routinely used in propellant/explosive formulations) poses a considerable risk in the initial process of dry mixing the plasticiser, binder and filler, as is conventional in solid propellant manufacture. The low F of F value excludes the use of CL20 in large scale propellant manufacture in some explosive companies. Thus, the manufacturer is challenged with the task of providing a safe process by which HNIW can be incorporated into explosive and propellant materials whilst having minimal effect on the overall performance characteristics of the end product.

The invention relates to an intermediate material for a propellant composition, the intermediate material being in powder form and comprising from 90 to 99 weight percent of a particulate energetic crystalline material and from 1 to 10 weight percent of an energetic plasticiser material, the energetic plasticiser material substantially coating the individual particles of the energetic crystalline material.

In the first aspect, the invention is an energetic material comprising an energetic crystalline material substantially coated in an energetic plasticiser material.

Preferably the energetic crystalline material is particulate, the energetic plasticiser substantially coating individual particles of the energetic crystalline material.

The energetic material is advantageously in powder form, the powder comprising particles of energetic crystalline material substantially coated in an energetic plasticiser material.

Advantageously the energetic material comprises from 90 to 99% by weight of an energetic crystalline material and from 1 to 10% by weight of an energetic plasticiser material.

The inventors have found that the combination of just a small quantity of energetic plasticiser material to the energetic crystalline material prior to incorporation into the bulk plasticiser, binder and filler mixture of an explosive or propellant composition has two unexpected and advantageous effects. Firstly, plasticiser addition leads to a reduction in the friction sensitivity of the energetic crystalline material to equivalent or less than that of many commonly used energetic filler materials such as ammonium perchlorate and secondly, the plasticiser addition also results in reduced ferocity of response on stimulation . The resultant novel intermediate of the energetic crystalline material and plasticiser can then be more safely used as a starting material for the dry mixing/blending/curing processes previously described used in the manufacture of known propellant and explosive compositions. These novel intermediate, plasticiser added, energetic crystalline material products are also more safely handled and transported than the pure energetic crystalline material.

In one particular method in accordance with the present invention, to manufacture an energetic material comprising an energetic crystalline material/energetic plasticiser mix, desirably the energetic crystalline material and energetic plasticiser material are mixed via a wet mixing process with the plasticiser material being added to, for example, water wet HNIW. The inherent characteristics of wet mixing reduces the friction arising within the mixture during the mixing process and thus minimises the risk of explosive reaction in the energetic crystalline material by friction stimuli. After mixing, the water wet, plasticised energetic crystalline material mix can be left to dry to a powdery state, the resultant dry powder formed being finely coated with the energetic plasticiser component. The resultant energetic crystalline material/energetic plasticiser mixture formed is a relatively friction insensitive energetic material when compared against pure, dry energetic crystalline material.

The inventors have found that the combination of just a small quantity of plasticiser material to an energetic crystalline material such as HNIW in manufacture of an explosive or propellant composition has an unexpected and advantageous effect of reducing the friction sensitivity of HNIW to equivalent or less than that of commonly used energetic filler materials such as Ammonium perchlorate or HMX. The resultant novel intermediate products manufactured by this desensitisation method can then be more safely used as a starting material for the dry mixing/blending/curing processes conventionally used in the manufacture of known propellant and explosive compositions. These novel intermediate products are also more safely handled and transported than the pure product. Another unexpected yet advantageous characteristic of these novel materials is that, once initiated, they display a reduced ferocity of response compared to that of the pure product.

The energetic plasticiser is preferably selected from the group comprising Butane Triol trinitrate (BTTN), Trimethylanol ethane trinitrate (TMETN), Diazidonitrazapentane (DANPE), Glycidyl Azide Polymer (Azide Derivative) (GAP Azide), Bis(2,2-dinitropropyl)acetal / bis(2,2-dinitropropyl)formal (BDNPA/F) or mixtures of two or more of these plasticisers. As well as bringing about the desired desensitisation effect, these plasticisers add energy to the propellant system compared to the use of inert analogues. As a consequence, the intermediate material produced has a higher energy density compared to inert analogues : this is a desirable characteristic of materials for use in rocketry / explosive programs as all constituents of the subsequent explosive / propellant formulation manufactured using the intermediate contribute energetically to the final formulation. The use of energetic crystalline materials desensitised with energetically inert plasticisers would have comparatively less energy than that of the proposed, energetic plasticisers formulations.

The energetic plasticiser material may comprise 100% of any of the plasticisers listed above, mixtures of those plasticisers listed above or optionally may be a blend of energetic plasticiser and a binder material (e.g. Poly(3-Nitratomethyl-3-

Methyloxetane) (PolyNIMMO), Poly Glycidyl Nitrate (PolyGLYN) or Glycidyl Azide Polymer (GAP)) of proportions encompassing from minimum quantity of 10% by weight plasticiser to 90% binder, to 100% plasticiser to 0% binder. The term "energetic plasticiser material" as referred to hereinafter should be construed accordingly with the above description.

Preferably, the novel energetic material will comprise between 1% and 5% by weight of energetic plasticiser material and most preferably between 3% and 5% by weight of energetic plasticiser material.

For mixed binder / plasticiser systems, preferably the energetic plasticiser material will comprise between 30% and 100% energetic plasticiser and 70% to 0% binder. Most preferably the plasticiser content will be in the range 60% to 100%.

Thus the present invention provides a method for manufacture of a highly energetic, intermediate material based on a energetic crystalline material desensitised for safe incorporation into propellant or explosive formulations.

In a second aspect, the present invention provides a method for manufacture of a propellant material containing an energetic crystalline material comprising;

(i) mixing 1 to 10% by weight of an energetic plasticiser material with 99 to 90% by weight of the energetic crystalline material,

(ii) mixing and/or blending the resultant product of step (i) with additional quantities of plasticiser and binder material as appropriate for the end application of the propellant material,

(iii) curing the resultant product of step (ii).

The energetic plasticiser material preferably contains a plasticiser selected from Butane Triol trinitrate (BTTN), Trimethylanol ethane trinitrate (TMETN), Diazidonitrazapentane (DANPE), Glycidyl Azide Polymer (Azide Derivative) (GAP Azide), Bis(2,2 - dinitropropyl) acetal / bis (2,2 - dinitropropyl) formal (BDNPA/F) or mixtures of two or more of these plasticisers.

In a third aspect the invention is an explosive or propellant composition made from a an energetic material comprising;

(i) from 90 to 99% by weight HNIW; and

(ii) from 1 to 10% by weight of an energetic plasticiser material comprising a plasticiser selected from the group comprising; Butane Triol trinitrate (BTTN), Trimethylanol ethane trinitrate (TMETN), Diazidonitrazapentane (DANPE), Glycidyl Azide Polymer (Azide Derivative) (GAP Azide), Bis(2,2-dinitropropyl)acetal / bis(2,2-dinitropropyl)formal (BDNPA/F), or mixtures of two or more of these components.

In order to more fully illustrate the novel methods, products and applications of this invention and their associated advantages, experimental data for some specific embodiments of the invention are now given by way of exemplification only. Although all analyses were carried out using Epsilon form HNIW, it is anticipated that this method of desensitisation would be effective on other crystal polymorphs of HNIW as well as known energetic crystalline materials such as cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX).

1) Rotary friction testing of HNIW in the Epsilon crystal form was carried out and a Figure of Friction (FofF) = 0.7 was achieved. The sample response during testing was a violent report and flash.

2) 0.25g of TMETN stabilised with 1% 2-Nitrodiphenylamine (2NDPA) was added to 5g of dry Epsilon form HNIW and mixed. The material formed was a light orange powder. The material was assessed by rotary friction and the FofF achieved = 2.2. In addition to the reduction in friction sensitiveness, the violence of response was reduced from a violent report / flash for the pure HNIW material to a mild report without flash.

3) Replicate analysis of the formulation example given in example 2 were carried out with the substitution of TMETN with BTTN, a mixture of BTTN and TMETN, DANPE, GAP Azide, BDNPA/F, PolyNIMMO, PolyGLYN and GAP. All materials appeared as white / yellow powders. For these mixtures, the friction sensitiveness determined were established as given in Table 1.

Table 1

Sample	**FofF**
CL20 : TMETN	2.2
CL20 : BTTN	2.1
CL20 : BTTN / TMETN (50/50)	2.4
CL20 : GAP Azide	2.1
CL20 : DANPE	1.9
CL20 : PolyGLYN	2.2
CL20: PolyNIMMO	1.9
CL20 : GAP	1.6

4) Replicate analysis of the formulation given in example 2 were carried out but with the substitution of TMETN with mixed binder : plasticiser formulations.

All mixtures formed white / light yellow powders. For these mixtures, the friction sensitiveness determined were established as shown in Table 2:

Table 2

Solid	**Binder**	**Plasticiser**	**FofF**
CL20	PolyGLYN	GAP Azide	2.7
CL20	PolyGLYN	DANPE	2.5
CL20	PolyGLYN	BTTN / TMETN (80:20)	2.7
CL20	PolyGLYN	BDNPA/F	2.1
CL20	PolyNIMMO	GAP Azide	2.9
CL20	PolyNIMMO	DANPE	2.9
CL20	PolyNIMMO	BTTN / TMETN (80:20)	3.1
CL20	PolyNIMMO	BDNPA/F	2.4
CL20	GAP	GAP Azide	2.8
CL20	GAP	DANPE	2.7
CL20	GAP	BTTN / TMETN (80:20)	2.8
CL20	GAP	BDNPA/F	2.7

5) 40g of CL20 was wetted to 25% moisture content with deionised water and mixed thoroughly. 2g of TMETN (stabilised with 2% 2NDPA) was added and again mixed thoroughly. The final CL20 / water / TMETN / 2NDPA mixture was placed on the open bench to allow water evaporation and final water was removed under vacuum storage at 80°C for 2 hours). Friction sensitiveness assessment of the dry powder formed was carried out and an FofF = 2.4 determined.

CLAIMS:

1. An intermediate material for a propellant composition, the intermediate material being in powder form and comprising from 90 to 99 weight percent of a particulate energetic crystalline material and from 1 to 10 weight percent of an energetic plasticiser material, the energetic plasticiser material substantially coating the individual particles of the energetic crystalline material.

2. An intermediate material as claimed in claim 1, wherein the amount of energetic plasticiser material is between 1 and 5 weight percent.

3. An intermediate material as claimed in claim 2, wherein the amount of energetic plasticiser material is between 3 and 5 weight percent.

4. An intermediate material as claimed in any one of claims 1 to 3, wherein the energetic plasticiser material is Butane Triol trinitrate (BTTN), Trimethylanol ethane trinitrate (TMETN), Diazidonitrazapentane (DANPE), Glycidyl Azide Polymer (Azide Derivative) (GAP Azide), Bis(2,2-dinitropropyl)acetal/ bis(2,2-dinitropropyl)formal (BDNPA/F), or a mixture thereof.

5. An intermediate material as claimed in any one of claims 1 to 4, wherein the energetic crystalline material is hexanitrohexaazaisowurtizane.

6. An intermediate material as claimed in any one of claims 1 to 5, which also comprises a binder.

7. An intermediate material as claimed in claim 6, wherein the proportion of energetic plasticiser material and binder by weight is from 10% to 100% energetic plasticiser and 90% to 0% binder.

8. An intermediate material as claimed in claim 6 or 7, wherein the binder is an energetic binder.

9. An intermediate material as claimed in claim 6 or 7, wherein the binder is poly(3-nitratomethyl-3-methyloxetane) (PolyNIMMO), polyglycidyl nitrate (PolyGLYN), or glycidyl azide polymer (GAP).

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