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(54) HIGH PERFORMANCE COMPOSITE PYROTECHNIC PRODUCT WITHOUT PB IN ITS COMPOSITION, AND PREPARATION THEREOF

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(57) ABSTRACT

A high performance composite pyrotechnic product without lead in its composition, and that can be obtained on an industrial scale without encountering a problem of potlife for the intermediate paste, the product containing organic energetic charges and a combustion catalyst in a plasticized binder including a cured energetic polymer and at least one energetic plasticizer. In characteristic manner, the cured energetic polymer consists of a glycidyle azide polymer (GAP) having number average molecular weight (Mn) lying in the range 700 g/mol to 3000 g/mol, cured via its hydroxyl terminal functions with at least one curing agent of polyisocyanate type; and the combustion catalyst consists of bismuth citrate.

HIGH PERFORMANCE COMPOSITE PYROTECHNIC PRODUCT WITHOUT PB IN ITS COMPOSITION, AND PREPARATION THEREOF

[0001] The present invention relates to composite pyrotechnic products that are suitable in particular for use as solid propellants for propulsive loads of rocket engines. More precisely, the invention relates to composite pyrotechnic products containing a high content of organic energetic charges in an energetic binder. Said products are particularly advantageous in that their composition does not contain any lead, in that they provide high performance, in particular in terms of burn rate, and in that the potlife (see definition below) of their precursor mixture (prior to curing) is long (thereby greatly facilitating obtaining such products on an industrial scale).

[0002] A solid propellant of composite type includes powder solid charges (oxidizing charges, and possibly also reducing charges), together with various additives, in particular feasibility additives and performance additives, in a binder that is generally plasticized (a generally plasticized and optionally energetic polymer matrix that is solid—i.e. a polymer that is cured).

[0003] The binder is obtained from a liquid polymer that is “curable”, having chemically reactive terminations suitable for being cured by at least one curing agent (having at least two functions) that is itself also liquid. In general, there are introduced into such a liquid polymer, in an appropriate order, at least one plasticizer and the other ingredients of the propellant, with the exception of said at least one curing agent (and with the exception of at least one curing catalyst, if use is made of such an at least one curing catalyst (generally very sensitive to moisture)), and then finally said at least one curing agent (and said at least one curing catalyst if one is used). The polymer with charges is then heat-treated (“baked”) at a temperature that is compatible with the energetic materials present (the charges a minima). Together with the present plasticizer(s), the cured polymer constitutes the plasticized binder that coats all the ingredients, and in particular the powder charges, so as to end up forming a solid body.

[0004] The method presently implemented for fabricating such composite pyrotechnic products in the form of blocks is a discontinuous method, referred to as a “batch” method, consisting in preparing a certain quantity of paste, in casting that quantity (or at least a portion of it) into a certain number of structures (at least one structure), and in applying heat treatment to the load(s) obtained in this way (in order to cure the polymer). In an initial step, the various ingredients are thus introduced in an appropriate order, and then they are carefully mixed over a long period under very specific conditions of temperature and of pressure (generally under a partial vacuum). For the following step, the mixture, which is thus in the form of a paste, is cast into at least one structure (said structure possibly being used together with tooling for shaping within the structure). The assembly is then subjected to heat treatment (baking) in order to cure (harden) the polymer. In most circumstances, the structure constitutes the actual casing of the load.

[0005] The at least one curing agent (and the at least one curing catalyst, if any) is/are introduced into the mixture towards the end of the mixing step. Specifically, once insertion starts, the paste—which is already naturally more or less viscous, depending on the nature of the polymer, on the content of charges, . . . , —begins to cure (to “harden”). Thus, casting can take place during only a limited length of time, referred to as the “potlife”, during which the mixture remains sufficiently fluid to be cast. For industrial working, it is essential for the potlife of the paste to be long enough (in order to have enough time for the various casting operations).

[0006] The potlife of a propellant paste is evaluated by measuring how the viscosity of said paste varies over time. It is considered that from a viscosity greater than 1.5 kPa·s =15 kPo (15kP), a propellant paste is no longer “castable”, and that a time shorter than 15 hours (h) for reaching this viscosity prevents any industrialization of the method. Paste having viscosity less than or equal to 1.5 kPa·s =15 kPo at the end of 15 h is thus the condition (both necessary and sufficient) that ensures that said paste is castable under industrial conditions. Naturally, the person skilled in the art understands that the potlife of a paste depends on the exact conditions (of temperature and pressure) under which said paste is cast.

[0007] In order to increase the burn rate of a solid propellant, it is known to add agents in the composition of said solid propellant that act as combustion catalysts (they are also referred to as ballistic catalysts). Organometallic salts of lead and oxides of lead have been used for this purpose in the past. Because of its toxicity, lead has more recently been replaced by bismuth; which is why salts and oxides of bismuth are used as combustion catalysts in solid propellants.

[0008] Patent application FR 2 727 401 thus describes the use of bismuth salts such as bismuth p-resorcylates, bismuth γ-resorcylate, bismuth salicylate, bismuth citrate, bismuth stearate, and also the use of bismuth oxide, as combustion catalysts for double base solid propellants (nitrocellulose and at least one nitric ester such as nitroglycerin) or composite double base solid propellants (charges in an energetic binder based on a nitric ester).

[0009] Nevertheless, the use of those novel combustion catalysts presents a drawback insofar as said novel combustion catalysts are also curing catalysts, and so using them shortens potlife (see above).

[0010] U.S. Pat. No. 6,168,574 confirms that the presence of bismuth salts, most particularly the presence of bismuth salicylate and the presence of bismuth β-resorcylate, in the composition of a composite propellant (having an energetic binder (of nitramine type: ORP-2 (see below)) or a non-energetic binder (polyglycol adipate (PGA), caprolactones), cured by a polyisocyanate) leads to a significant shortening of potlife, since the bismuth salt (combustion catalyst) also acts as a curing catalyst. Said patent proposes a “processing trick” for limiting this shortening of potlife. It proposes introducing the bismuth salt in a propellant paste (prepared upstream) that is cooled to about 16° C. (60° F.) instead of being at a temperature in the range 32° C.-38° C. (90° F.-100° F.) approximately as in the conventional method. It can be understood that the greater increase in the viscosity of the paste that is inherent to such greater cooling, inevitably complicates subsequent implementation of the method. Specifically, implementing a method that includes putting the paste at a low temperature limits choices concerning the nature of polymers that are suitable for binder precursors. Said polymers must be capable of being cast at a temperature that is that low.

[0011] U.S. Pat. No. 6,168,677 confirms the teaching of patent U.S. Pat. No. 6,168,574. It describes and evaluates composite propellants having an energetic binder cured with a polyisocyanate and containing in their composition bismuth salicylate and/or bismuth citrate, as a ballistic catalyst. The energetic binders described are binders of nitramine type, obtained from (acid) polymers of ORP-2 type (poly (diethylenegylcol-4,8-dinitrazuandecanoate) and of 9DT-NIDA type (diethylenegylcol-triethylenegylcol-nitraminodiacetic terpolymer). Such polymers can be cast at low temperature, at 60° F.≈16° C. (see Table 10 of U.S. Pat. No. 6,168,677).

[0012] Until now, the person skilled in the art has always sought a highly energetic high performance propellant that incorporates in its composition a ballistic catalyst that is not toxic (lead free), that can be obtained on an industrial scale with a paste that presents a potlife that is sufficiently long, and that can be worked under conditions that are advantageous, and simple, in particular in terms of managing temperature.

[0013] In such a context, the Applicant proposes a novel composite propellant having a specific energetic binder (comprising a specific energetic polymer (GAP) cured with at least one polyisocyanate), and containing a specific combustion catalyst (bismuth citrate) in its composition. This new composite propellant, of composition that does not contain lead, presents high performance in energy terms (in particular, it presents a fast burn rate) and its method of preparation is particularly advantageous. The Applicant has the o merit of having selected a pair comprising a precursor polymer for an energetic binder and a combustion catalyst that, when used conventionally with polyisocyanate(s), plasticizer(s) and organic energetic charges, leads to a propellant that, while it is in the form of a paste prior to curing, presents a potlife close to the potlife of a similar propellant that does not contain a is combustion catalyst in its composition or that contains lead citrate as a combustion catalyst in its composition; with this applying at a temperature in the range 35° C.-55° C. (which temperature, higher than ambient temperature, is entirely suitable for "simple" working of the method of preparing said propellant (see below)).

[0014] In a first aspect, the present invention thus provides novel composite pyrotechnic products that are highly energetic and that do not contain lead in their composition. They are of the type having a cured energetic binder containing organic energetic charges. More precisely, they contain organic energetic charges and a combustion catalyst in a plasticized binder comprising a cured energetic polymer and at least one energetic plasticizer. In characteristic manner:

[0015] said cured energetic polymer consists of a glycidyl azide polymer (GAP) having number average molecular weight (Mn) lying in the range 700 grams per mole (g/mol) to 3000 g/mol, cured via its hydroxyl terminal functions with at least one curing agent of polyisocyanate type; and

[0016] the combustion catalyst consists of bismuth citrate.

[0017] The structure of composite pyrotechnic products of the invention thus associates, in characteristic manner, a specific binder and a specific combustion catalyst. This association is found to be particularly advantageous with reference to the specifications, which include two stipulations that, a priori, are contradictory (because combustion catalysts are generally also curing catalysts (see above)): the product should present highly energetic performance (fast burn rates) (requiring the presence of an effective quantity of combustion catalyst); and the method of obtaining it should be easy (most particularly with reference to the problem of the lifetime ("potlife") of the paste that is to be cured).

[0018] The nature of the binder (the nature of its precursor polymer) thus constitutes one of the key elements for the composition of composite pyrotechnic products of the invention.

[0019] It should be observed in passing that the term "a" glycidyl azide polymer(=precursor polymer for the binder) should be understood as "at least one" glycidyl azide polymer throughout the present specification. Specifically, the ambit of the invention does not in any way exclude a mixture of at least two glycidyl azide polymers (presenting different molecular weights (in the range 700 g/mol to 3000 g/mol) and/or different degrees of branching) being used as a precursor polymer for the binder in the products of the invention.

[0020] The energetic polymer selected as the precursor for the binder of products of the invention is thus an azide polymer, a glycidyl azide polymer (GAP) that presents hydroxy terminal functions (a hydroxytelechelic GAP); giving it: 1) its energetic properties; and 2) its ability to be cured with curing agents of the polyisocyanate type.

[0021] Said polymer has a suitable molecular weight (in particular with reference to its (liquid) consistency and to the consistency of its mixture essentially with the charges (organic energetic charges) and with reference to the relative curing agent(s) content of the cured binder), a number average molecular weight (Mn) lying in the range 700 g/mol to 3000 g/mol, and advantageously lying in the range 1700 g/mol to 2300 g/mol.

[0022] The inventors have the merit of having identified (selected) this type of (precursor polymer of) binder, as being entirely suitable for use with bismuth citrate as a combustion catalyst.

[0023] Curing agents of the polyisocyanate type (having at least two functions) that are suitable for curing such a hydroxytelechelic glycidyl azide polymer (GAP) are themselves known. They may in particular be di- or tri-isocyanates. Advantageously they are liquid poly-isocyanates selected from toluene diisocyanate (TDI), isophorone diisocyanate (IDPI), methylene dicyclohexyl diisocyanate (MDCI), hexamethylene diisocyanate (HDI), the trimer of said hexamethylene diisocyanate (in particular as sold by the supplier Bayer under the trade name Desmodur® N 3300), biuret trihexane isocyanate (BTHI), 3,5,5-trimethyl-1,6-hexamethylene diisocyanate, and mixtures thereof. In particularly preferred manner, use is made of hexamethylene diisocyanate trimer.

[0024] Said curing agents are conventionally used in necessary and sufficient quantity to ensure that the polymer is cured (but not excessively so as to avoid polluting the resulting cured product). They are conventionally used in a quantity such that the bridging ratio of NCO (from the curing agent) over OH (of the polymer) lies in the range 0.8 to 1.4, and is advantageously 1.

[0025] The cured energetic polymer generally represents 10% to 14% by weight of the total composition of composite pyrotechnic products of the invention. The energetic polymer itself generally constitutes 8% to 12% by weight, with the at least one curing agent representing about 2% by weight.

[0026] It is clearly understood that the nature of the binder (of its precursor polymer) is not of itself original, but that the advantage of the invention lies on associating (a precursor polymer for) such a binder with a specific combustion catalyst.

[0027] In conventional manner, the energetic binder is associated with at least one energetic plasticizer. The energetic plasticizer(s) in question is/are advantageously of the nitrate and/or nitramine type. The energetic plasticizer(s) in question is/are most advantageously selected from diethylene glycol dinitrate (DEGDN), triethylene glycol dinitrate (TEGDN), butanetriol trinitrate (BTTN), trimethylolethane trinitrate (TMETN), a mixture of 2,4-dinitro-2,4-diaza-pentane, of 2,4-dinitro-2,4-diaza-hexane, and of 3,5-dinitro-3,5-diaza-heptane (and most particularly DNDA 5.7), nitrato ethyl nitramines (and in particular methyl-2-nitratoethyl nitramine (methylNENA), and ethyl-2-nitratoethyl nitramine (ethylNENA)), and mixtures thereof.

[0028] The plasticizer(s) of pyrotechnic products of the invention generally represent(s) 10% to 30% by weight, more generally 15% to 25% by weight, of the total composition of said products.

[0029] The energetic charges that are present are organic charges.

[0030] The organic energetic charges in question are not themselves original. They are already known organic energetic charges and for the most part they are already conditioned in the prior art in cured energetic polymer binders (in particular of the GAP type). Advantageously, they comprise hexogen (RDX), octogen (HMX), hexanitrohexaazaisowurtzitane (CL20), nitroguanidine (NGU), ethylene dinitramine (EDNA), N-guanylurea dinitramide (FOX 12 (GUDN)), 1,1-diamino-2,2-dinitro ethylene (FOX 7 (DADE)), bis(triaminoguanidinium)-5,5'-azotetrazolate (TAGZT), dihydrazinium 5,5'-azotetrazolate (DHDZT), 5,5'-bis(tetrazolyl)hydrazine (HBT), bis(2,2-dinitropropyl) nitramine (BDNPN), and nitropyrazole charges, or a mixture of such (organic energetic) charges.

[0031] Within composite pyrotechnic products of the invention, there is thus to be found a type of energetic charge that is advantageously selected from the above list, or a mixture of at least two types of energetic charge that are advantageously selected from the above list. In preferred manner, there are energetic RDX charges therein.

[0032] Organic energetic charges are conventionally in the form of solid grains that are homogeneously distributed within the plasticized cured binder. In known manner, such solid grains advantageously present a plurality of grain size distributions.

[0033] The organic energetic charges of pyrotechnic products of the invention generally constitute 50% to 70% by weight, more generally 55% to 65% by weight of the total composition of said products. It can be understood that said products have high charge contents.

[0034] The presence of inorganic energetic charges within the plasticized binder of pyrotechnic products of the invention is not to be totally excluded. But in any event, such inorganic energetic charges, if present, should be present in small quantity (<4% by weight). They may be considered as being additives (see below). Their presence can be advantageous, with respect to the ballistic properties of the product; nevertheless, they must not be responsible for forming large amounts of combustion smoke or light.

[0035] In contrast, the presence of metallic charges within the plasticized binder of pyrotechnic products of the invention is generally to be excluded. Specifically, on combustion, such metallic charges are liable to generate particles.

[0036] The nature of the combustion catalyst that is present thus constitutes another of the key elements in the composition of composite pyrotechnic products of the invention. Said combustion catalyst consists of bismuth citrate. Because of its reduced toxicity, said bismuth citrate advantageously takes the place of prior art salts and oxides of lead. Furthermore, and in surprising manner, said specific combustion catalyst constituted by bismuth citrate within the specific plasticized binder of pyrotechnic products of the invention has a positive effect on combustion (most particularly on burn rate) without giving rise to problems upstream during preparation of the product (the preparation method being “easy” to perform, generally at “constant temperature” until the polymer cures, and in any event not including any significant cooling (of the type described in patents U.S. Pat. Nos. 6,168,574 and 6,168,677) and without any problem of managing potlife). On this topic, the reader is invited to consider the results in Table 2 below.

[0037] Bismuth citrate (the combustion catalyst) is generally present in the composition of pyrotechnic products of the invention at a content by weight in the range 1% to 6%, very generally at a content by weight in the range 3% to 5%.

[0038] In their binders (cured precursor polymer), composite pyrotechnic products of the invention are also likely to contain, and generally do contain, not only the plasticizer (s), the organic energetic charges, and the (specific) combustion catalyst, but also at least one additive. It is more accurate to say at least one “other” additive, since combustion catalysts generally constitute additives. The combustion catalysts are presently kept separate from the other additives, insofar as they lie behind the technical problem presently under consideration and the (specific) combustion catalyst that is selected constitutes a key element of products of the invention.

[0039] Among additives that are advantageously present, preference may be given to the following conventional additives: curing catalysts and stabilizer agents for the energetic plasticizer(s) that is/are present. Thus, in an advantageous variant, composite pyrotechnic products of the invention thus include in their composition, in addition to the cured polymer (GAP), the plasticizer(s), the organic energetic charges, and the combustion catalysts (bismuth citrate), at least one additive; said at least one additive comprising at least one curing catalyst and/or at least one stabilizer agent for the plasticizer(s) that is/are present. Said at least one polymerization catalyst may in particular be selected from triphenylbismuth and dibutyl tin laurate (DBTL). When present, it is generally at a content that does not exceed 100 parts per million (ppm). Said at least one stabilizer agent for stabilizing the plasticizer(s) that is/are present may in particular consist of at least one aromatic amine, such as 2-nitrodiphenylamine (2-NDPA), and N-methyl para nitroanline (MNA). When present, it is generally present at a content of about 1% by weight.

[0040] Other additives that may be present in the composition of composite pyrotechnic products of the invention may in particular consist of inorganic energetic charges (see above), and in one or more working agents (processing auxiliary(ies)), Said agent(s) is/are generally present at a content in the range 1% to 2% by weight.

[0041] The additives that are optionally present (and in the light of the above description, it can be understood that several types of additive are generally, present) generally represent no more than 4% by weight of the composition of composite pyrotechnic products of the invention, Most generally, they represent 0.1% to 4% by weight of the composition of composite pyrotechnic products of the invention.

[0042] In the light of the above description, it can be understood that the composite pyrotechnic products of the invention are not of a type that is novel but that they are novel by associating, in their composition, a specific binder (GAP cured at least by polyisocyanate) with a specific combustion catalyst (bismuth citrate).

[0043] In the context of an advantageous variant, the composition of composite pyrotechnic products of the invention, expressed as percentages by weight, thus comprise:

[0044] 50% to 70%, advantageously 55% to 65% of organic energetic charges; and

[0045] 10% to 14% of energetic polymer (of the hydroxytelechelic GAP type cured via its hydroxy terminal functions by at least one polyisocyanate);

[0046] 10% to 30%, advantageously 15% to 25% of at least one energetic plasticizer;

[0047] 1% to 6%, advantageously 3% to 5% of bismuth citrate; and

[0048] 0 to 4%, advantageously 0.1% to 4% of at least one additive.

[0049] It can be understood that the above-mentioned advantageous ranges may perfectly well be considered independently of one another, Preferably, they are considered in combination with one another.

[0050] In the context of this advantageous variant, the composition is generally free of any other ingredient (in particular of any metallic charge), and it thus consists of the ingredients listed above, present in the quantities specified above.

[0051] The great advantage of products of the invention can clearly be seen from the above description. The products are advantageous per se (in terms of ballistic performance, and also because of their mechanical properties, and the small signature of the plume they generate during propulsive combustion (discretion)), and insofar as the potlife of the (precursor) paste containing the ingredients is close to that of the paste for a similar propellant that does not include bismuth citrate. More generally, there is no difficulty in carrying out the preparation of the products of the invention, and such carrying out is found to be "optimized" in terms of temperature management.

[0052] In a second aspect, the present invention thus provides a method of preparing a composite pyrotechnic product, as described above. The method comprises:

[0053] preparing a homogeneous paste by:

[0054] a) incorporating, with stirring, at a temperature lying in the range 35° C. to 55° C., in a suitable glycidyl azide polymer (hydroxytelechelic GAP presenting a number average molecular weight as specified above), at least one energetic plasticizer, organic energetic charges, and other ingredients constituting the desired composite pyrotechnic product (including the specific combustion catalyst: bismuth citrate) with the exception of any curing agent and any curing catalyst; and

[0055] b) stirring the resulting mixture under a partial vacuum at a temperature lying in the range 35° C. to 55° C. (advantageously at said temperature);

[0056] under a partial vacuum, at a temperature lying in the range 35° C. to 55° C. (advantageously at said temperature), incorporating in said resulting homogeneous paste, said at least one curing agent and optionally at least one curing catalyst, followed by stirring the resulting mixture;

[0057] casting said resulting stirred mixture(=the mixture that is obtained) in at least one structure; and

[0058] heat treating said resulting stirred mixture (that has been stirred) as cast in said at least one structure.

[0059] The specified partial vacuum is for degassing the above medium to which it is applied. The vacuum is generally 10 millimeters of mercury (mmHg). It should be observed in passing that it is not necessarily constant in value.

[0060] The heat treatment (for curing the hydroxytelechelic GAP) is generally performed at a temperature lying in the range 30° C. to 60° C. (30° C.≤T≤60° C.) for several days.

[0061] The method may be considered as a method by analogy, but in characteristic manner, because of the specific nature of (the precursor polymer for) the binder and because of the specific nature of the combustion catalyst, its initial steps are performed at temperatures (advantageously at one temperature) in the range 35° C. to 55° C. (35° C.≤T(s)≤55° C.), without cooling, and without any potlife problem for said polymer.

[0062] The invention is illustrated below by the following examples. More precisely, there follow Examples A, B1, and B2 illustrating the prior art, Examples 1 and 2 illustrating the invention, and comparative Examples C1 and C2.

[0063] Examples 1 and 2 relate to propellants of the invention that include in their composition hexogen (RDX) charges, a binder based on an energetic polymer of hydroxytelechelic PAG type (sold by the supplier Eurenco (Mn (number average molecular weight)=1900 (g/mol) that has been cured (by hexamethylene diisocyanate trimer sold by the supplier Bayer under the trade name Desmodur® N 3300), and plasticized (by a mixture of two energetic plasticizers (BTTN/TMETN; 30/70 (% by weight), stabilizer agents for said plasticizers (MNA/2-NDPA; 75/25 (% by weight)), and bismuth citrate as ballistic catalyst (at a content by weight of 1% in Example 1 and a content by weight of 4% in Example 2).

[0064] Said propellants of Examples 1 and 2 have been compared with reference propellants, one of which (Ref. 1) had no ballistic catalyst in its composition (Example A), and the other of which (Ref. 2) had lead citrate as ballistic catalyst in its composition at contents by weight of 1% (Example B1) and of 3.5% (Example B2).

[0065] Two comparative examples are also described with propellants similar to the propellant of Example 2 of the invention, but including, as ballistic catalysts, bismuth subsalicylate (C1) and bismuth carbonate (C2), replacing bismuth citrate.

[0066] The compositions of these propellants (more precisely the compositions of their pastes prior to curing) are set out in Table 1 below.

[0067] The same ingredients were naturally used for all of the examples. Concerning the RDX charges, they were constituted by 68% by weight of an RDX having a grain size class of 0-100 micrometers (μm) and 32% by weight of RDX having a grain size class of 2.5 μm-5 μm.

TABLE 1

Ingredients (% by weight)			Propellants (% by weight)						
			Ref. 1	Ref. 2		Examples		Comparative examples	
			A	B1	B2	Ex. 1	Ex. 2	C1	C2
Plasticized binder	Energetic polymer	PAG	10.63	10.63	9.63	10.63	9.63	9.63	9.63
	Curing agent	Desmodur ® N 3300	2.01	2.01	2.01	2.01	2.01	2.01	2.01
	Plasticizers	BTTN/TMETN	20.7	20.7	19.7	20.7	19.7	19.7	19.7
	Plasticizer stabilizer agents (additive)	MNA/2-NDPA	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Charges	Organic energetic charges	RDX	64	63	62.5	63	62	62	62
Combustion "additive"	Combustion catalyst	Pb citrate		1	3.5				
		Bi citrate				1	4		
		Bi subsalicylate						4	
		Bi carbonate							4
Other additive	Processing auxiliaries		1.86	1.86	1.86	1.86	1.86	1.86	1.86

[0068] Composite pyrotechnic products (propellants) were thus prepared presenting the compositions by weight given in Table 1 above. For that purpose, the method set out below was performed (see the following paragraph headed "Preparation").

[0069] Attention was paid to the pot lives of the propellant pastes (intermediates) that were prepared. Said potlife was determined by performing viscosity measurements as described below (see the paragraph below headed "Determining the potlife"). The results appear in the first portion of Table 2 below.

[0070] In its second portion, said Table 2 also contains the burn rate results as measured at different pressures, on the propellants as finally obtained.

Preparation

[0071] The following were introduced into a mixer: glycidyl azide polymer (GAP) as a binder precursor polymer; followed by the plasticizers (BTTN/TMETN) and the stabilizing agents (MMA/2-NDPA) for said plasticizers. The mixture was mixed for 15 minutes (min) at a temperature of 40° C.

[0072] Thereafter, the following were added to said mixture under stirring: the organic energetic charges (RDX) in portions; followed by the additives (other than the curing agent and catalyst (Desmodur® N 3330 and DBTL)); and the combustion catalyst. Stirring was then continued for 2 h 30 min, still at the temperature of 40° C. and under a vacuum of 10 mmHg (to enable the medium to degas), in order to obtain a homogeneous paste.

[0073] The curing catalyst (DBTL (55 ppm)) was then added to said homogeneous paste and the medium continued to be stirred for 30 min prior to adding the curing agent for the binder. Said curing agent (Desmodur® N 3300) was finally added, and the medium continued to be stirred for 15 min (still at 40° C. and under a vacuum).

[0074] Propellant paste was thus prepared in 2 kilogram (kg) batches.

[0075] A sample was taken of each of the propellant pastes as prepared in that way in order to determine potlife.

[0076] The remainder of each of the prepared propellant pastes was then cast into a suitable structure and subjected to the following heat treatment: baking for 75 h at a temperature of 50° C.

Determining the Potlife of the Pastes

[0077] Potlife was determined by measuring the viscosity of the propellant paste in question (containing the curing agent and the curing catalyst) over time, by using a Brookfield viscosity meter (using the No. 3 body (mobile C) rotating at 1 revolution per minute (rpm)), at a temperature of 40° C. The time for the viscosity to reach 15 kPo was measured in order to determine whether the propellant satisfied the criterion for industrialization, i.e. whether the measured time was greater than 15 h.

TABLE 2

	Ref. 1	Ref. 2		Invention		Comparative examples	
	A	B1	B2	Ex. 1	Ex. 2	C1	C2
Combustion catalyst	/	Lead citrate		Bismuth citrate		Bismuth subsalicylate	Bismuth carbonate
% by weight	0	1	3.5	1	4	4	4
Time for paste viscosity to reach ≥15 kPo at 40° C.	>24 h	>24 h	>24 h	>24 h	>16 h	<1 h	<1 h
	Ballistic properties						
Pressure (MPa)	Burn rate (millimeters per second)						
7	6.6	9.5	15.6	8.9	12.7		
10	8.8	11.7	16.4	11.3	14.8		
13	11.1	14.0	17.9	13.6	16.2		
18	15.3	17.6	20.4	17.5	18.4		

[0078] The following comments are made on the topic of the results of Table 2.

Potlife

[0079] As expected, pastes of the reference propellants, without ballistic catalyst (Example A) or containing lead citrate as ballistic catalyst (Examples B1 and B2) reached the viscosity value of 15 kPo after longer than 24 h, thus satisfying the criterion for industrial castability.

[0080] The propellant paste of Example 1 (of the invention) incorporating bismuth citrate at a content by weight of 1% presented castability properties equivalent to those of the propellants of reference A (no ballistic catalyst) and B1 (containing 1% by weight of Pb citrate).

[0081] Example 2 (of the invention) shows that even with a high content by weight (4%) of bismuth citrate, the propellant paste conserved viscosity less than or equal to 15 kPo for at least 16 h, which is more than the minimum time of 15 h (required for performing the operations of casting the paste industrially).

[0082] The viscosity of the propellant pastes of the comparative Examples C1 and C2 exceeded the maximum acceptable viscosity value (15 kPo) in less than one hour (which is much less than the required 15 h). This shows that selecting the pair comprising PAG and bismuth citrate in accordance with the invention is particularly pertinent).

Burn Rates

[0083] Table 2 also shows that the ballistic catalyst (combustion catalyst), i.e. bismuth citrate, imparts burn rates to propellants of the invention as a function of pressure that are much greater than those of reference propellant A (without ballistic catalyst in its composition), and close to those propellants B1 and B2 of composition including lead citrate (toxic product) as the combustion catalyst.

1. A composite pyrotechnic product containing organic energetic charges and a combustion catalyst in a plasticized binder comprising a cured energetic polymer and at least one energetic plasticizer, wherein:

said cured energetic polymer consists of a glycidyle azide polymer (GAP) having number average molecular weight (Mn) lying in the range 700 g/mol to 3000 g/mol, cured via its hydroxyl terminal functions with at least one curing agent of polyisocyanate type; and

said combustion catalyst consists of bismuth citrate.

2. The composite pyrotechnic product according to claim **1**, wherein said glycidyle azide polymer (GAP) has number average molecular weight (Mn) lying in the range 1700 g/mol to 2300 g/mol.

3. The composite pyrotechnic product according to claim **1**, wherein said at least one energetic plasticizer is of the nitrate and/or nitramine type.

4. The composite pyrotechnic product according to claim **1**, wherein said organic energetic charges are selected from:

hexogen, octogen, hexanitrohexaazaisowurtzitane, nitroguanidine, ethylene dinitramine, N-guanylurea dinitramide, 1,1 -diamino-2,2-dinitro ethylene, bis(triaminoguanidinium)-5,5'-azotetrazolate, dihydrazinium 5,5'-azotetrazolate, 5,5'-bis(tetrazolyl)hydrazine, bis(2, 2-dinitropropyl) nitramine, and nitropyrazole charges, and mixtures of such charges.

5. The composite pyrotechnic product according to claim **1**, containing 1% to 6% by weight, of said bismuth citrate.

6. The composite pyrotechnic product according to of claim **1**, further containing at least one additive.

7. The composite pyrotechnic product according to claim **6**, wherein said at least one additive comprises at least one curing catalyst and/or at least one stabilizer agent for said at least one energetic plasticizer.

8. The composite pyrotechnic product according to claim **1**, wherein in that its composition contains the following, expressed in percentages by weight:

50% to 70% of said organic energetic charges;

10% to 14% of said cured energetic polymer;

10% to 30% of said at least one energetic plasticizer;

1% to 6%, of said bismuth citrate; and

0 to 4%, of at least one additive.

9. A method of preparing a composite pyrotechnic product according to claim **1**, comprising:

preparing a homogeneous paste by:

a) incorporating, at a temperature lying in the range 35° C. to 55° C., in said glycidyle azide polymer, said at least one energetic plasticizer, organic energetic charges, and other ingredients constituting said desired composite pyrotechnic product with the exception of any curing agent and any curing catalyst; and

b) stirring the resulting mixture under a partial vacuum at a temperature lying in the range 35° C. to 55° C.;

under a partial vacuum, at a temperature lying in the range 35° C. to 55° C., incorporating in said resulting homogeneous paste, said at least one curing agent and optionally at least one curing catalyst, followed by stirring the resulting mixture;

casting said stirred resulting mixture in at least one structure; and

heat treating said cast stirred resulting mixture in said at least one structure.

10. The composite pyrotechnic product according to claim **5**, containing 3% to 5% by weight of said bismuth citrate.

11. The composite pyrotechnic product according to claim **8**, wherein its composition contains, expressed in percentages by weight, 55% to 65% of said organic energetic charges.

12. The composite pyrotechnic product according to claim **8**, wherein its composition contains, expressed in percentages by weight 15% to 25% of said at least one energetic plasticizer.

13. The composite pyrotechnic product according to claim **8**, wherein its composition contains, expressed in percentages by weight, 3% to 5% of said bismuth citrate.

14. The composite pyrotechnic product according to claim **8**, wherein its composition contains, expressed in percentages by weight, 0.1% to 4% of said at least one additive.

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