(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 022 770 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
11.02.2009 Bulletin 2009/07

(21) Application number: **07741775.6**

(22) Date of filing: **17.04.2007**

(51) Int Cl.:
C06B 23/00 $^{(2006.01)}$
C06B 29/00 $^{(2006.01)}$
C06B 33/00 $^{(2006.01)}$
C06B 45/00 $^{(2006.01)}$
C06D 5/00 $^{(2006.01)}$
B60R 21/26 $^{(2006.01)}$
B60R 22/46 $^{(2006.01)}$
C06B 21/00 $^{(2006.01)}$
C06B 31/00 $^{(2006.01)}$
C06B 43/00 $^{(2006.01)}$
C06C 7/00 $^{(2006.01)}$
C06D 5/06 $^{(2006.01)}$
B60R 21/34 $^{(2006.01)}$

(86) International application number:
PCT/JP2007/058339

(87) International publication number:
WO 2007/123120 (01.11.2007 Gazette 2007/44)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

(30) Priority: **19.04.2006 JP 2006115153**

(71) Applicant: **Nipponkayaku Kabushikikaisha**
Tokyo 102-8172 (JP)

(72) Inventors:
- **SASAMOTO, Kouichi**
  Himeji-shi
  Hyogo 679-2123 (JP)
- **TANAKA, Yasuhiro**
  Himeji-shi
  Hyogo 679-2123 (JP)

(74) Representative: **Wibbelmann, Jobst**
Wuesthoff & Wuesthoff
Patent- und Rechtsanwälte
Schweigerstrasse 2
81541 München (DE)

(54) EXPLOSIVE COMPOSITION, EXPLOSIVE COMPOSITION MOLDED BODY, AND THEIR PRODUCTION METHODS

(57) The invention provides an explosive composition obtained by milling a fuel component and an oxidizer component with an aqueous emulsion of a hydrophobic tackifier and drying them, which is high in the water resistance and good in the extrusion moldability and cleanability of a shaping machine and less in the production problem. Also, the explosive composition according to the invention is preferable to be applied as a shaped body to a gas generating agent, an autoignition agent, an enhancer agent or the like. Further, the explosive composition shaped body according to the invention is particularly preferable to be used for a gas generator actuating an automobile safety device.

EP 2 022 770 A1

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] This invention relates to an explosive composition and an explosive composition shaped body as well as a method for producing the same, and concretely to an explosive composition suitable for use in a gas generator for actuating an automobile safety device such as an air bag, a seat belt pretensioner, a bonnet lifting device or the like.

RELATED ART

[0002] As the explosive composition for the gas generator, there are, for example, a gas generating agent, an enhancing agent, a priming composition, an autoiginition agent and so on. Among them, the gas generating agent, the enhancing agent and the autoignition agent are typically used as a shaped body, so that they are added with an adhesive (binder) dissolving in a solvent used such as water, an organic solvent or the like (JP-A-2000-95592). Also, there is known an extrusion-moldable priming composition using a water-soluble or water-expandable binder as an aqueous adhesive using water as a solvent (JP-A-2003-524565). Furthermore, there is known an explosive composition using an aqueous suspension of ethylene/vinyl acetate copolymer as an aqueous adhesive (JP-A-2003-238285). And also, there is known an explosive composition using a synthetic hydrotalcite as an inorganic binder (JP-A-2001-192288).

DISCLOSURE OF THE INVENTION

[0003] However, in case of the binder using the organic solvent as a solvent as disclosed in JP-A-2000-95592, there are drawbacks that it is necessary to take a care on the safeness and the regulation of emitting VOC (volatile organic compounds) should be satisfied. In case of the binder using water as a solvent as disclosed in JP-A-2000-95592 or JP-A-2003-524565, the safeness is good, but there are drawbacks that the hygroscopicity can not be lowered and the shaped bodies after shaping are fixed to each other. Furthermore, there are many problems in the production such as time-consuming cleaning due to the adhesion of chemicals to the shaping machine and the like. And also, there is a problem in the maintenance of the production device requiring a solvent for cleaning the shaping machine due to the adhesion of chemicals. In the composition as disclosed in JP-A-2003-238285, the shaped body can not be obtained even by the extrusion molding. The binder used in JP-A-2001-192288 is effective as a binder for tablet machinery, but is not suitable as a binder for extrusion molding and hence the extrusion-molded body can not be obtained.

[0004] The invention is made for solving the above problems and is to provide an explosive composition and an explosive composition shaped body which are good in the water resistance and less in the production problem as compared with the conventional ones. Also, it is another object of the invention to provide a method of producing the explosive composition and the explosive composition shaped body.

[0005] That is, the summary and construction of the invention are as follows.

[0006] 1. An explosive composition characterized by milling and drying a fuel component and an oxidizer component in the presence of an aqueous emulsion of a hydrophobic tackifier.

[0007] 2. The explosive composition according to the item 1, wherein a content of the hydrophobic tackifier is 2-15 mass%.

[0008] 3. The explosive composition according to the item 1 or 2, wherein the hydrophobic tackifier is at least one selected from the group consisting of a rubber-based tackifier, an acryl-based tackifier and a silicone-based tackifier.

[0009] 4. The explosive composition according to the item 3, wherein the hydrophobic tackifier is an acryl-based tackifier.

[0010] 5. The explosive composition according to the item 3 or 4, wherein the hydrophobic tackifier has a heat decomposition temperature of not lower than 200˚C.

[0011] 6. The explosive composition according to any one of the items 1-5, wherein the fuel component is a nitrogen-containing compound and/or boron.

[0012] 7. The explosive composition according to the item 6, wherein the nitrogen-containing compound is at least one selected from the group consisting of guanidine, tetrazole, bitetrazole, triazole, hydrazine, triazine, azodicarbonamide, dicyanamide and derivatives thereof and a nitramine compound.

[0013] 8. The explosive composition according to any one of the items 1-7, wherein the oxidizer component is at least one selected from the group consisting of a chlorate, a perchlorate, a nitrate and a basic nitrate.

[0014] 9. The explosive composition according to the item 8, wherein the oxidizer component is at least one selected from the group consisting of ammonium perchlorate, potassium perchlorate, sodium perchlorate, potassium nitrate, sodium nitrate, strontium nitrate and basic copper nitrate.

[0015] 10. The explosive composition according to any one of the items 1-9, which further contains at least one selected from a metallic powder, silicon nitride and a metal nitride.

[0016] 11. The explosive composition according to any one of the items 1-10, which further contains a surfactant.

[0017] 12. The explosive composition according to the item 11, wherein the surfactant is a nonionic surfactant having a HLB value of not more than 15.

[0018] 13. An explosive composition shaped body characterized by milling, shaping and drying a fuel component and an oxidizer component as described in any one of the items 1-9 in the presence of an aqueous emulsion of a hydrophobic tackifier.

[0019] 14. The explosive composition shaped body according to the item 13, wherein the shaped body is any of a gas generating agent, an autoignition agent and an enhancer agent.

[0020] 15. The explosive composition shaped body according to the item 13 or 14, wherein the shaped body is for an automotive safety device.

[0021] 16. The explosive shaped body according to any one of the items 13-15, wherein the shaped body has any of a granular form, a tablet form, a columnar form, a cylindrical form, a prismatic form, a porous cylindrical form and a porous prismatic form.

[0022] 17. The explosive composition shaped body according to any one of the items 13-16, which further contains at least one selected from a metallic powder, silicon nitride and a metal nitride.

[0023] 18. The explosive composition shaped body according to any one of the items 13-17, which further contains a surfactant.

[0024] 19. The explosive composition shaped body according to the item 18, wherein the surfactant is a nonionic surfactant having a HLB value of not more than 15.

[0025] 20. A method of producing an explosive composition, which comprises milling a fuel component and an oxidizer component with an aqueous emulsion of a hydrophobic tackifier and drying them.

[0026] 21. A method of producing an explosive composition shaped body, which comprises milling a fuel component and an oxidizer component with an aqueous emulsion of a hydrophobic tackifier and shaping, drying and solidifying them.

[0027] 22. The method of producing an explosive composition shaped body according to the item 17, wherein the shaping is an extrusion molding.

[0028] The explosive composition according to the invention is less in the adhesion of mutual shaped bodies after the shaping and easy in the disintegration of aggregated chemicals after the drying. Also, the resulting dry shaped body is good in the moisture absorption resistance and water resistance and suitable as an explosive composition for a gas generator actuating a moisture-proof automobile safety device. Furthermore, in the production of the explosive composition shaped body according to the invention, the hydrophobic tackifier is dispersed into water at an emulsion state for use as an aqueous emulsion, whereby the milled mass of the fuel component and oxidizer component becomes glutinous and facilitates the extrusion molding. Moreover, the milled mass hardly adheres to the production machine and also the cleaning of the machine after the production becomes easy.

BEST MODE FOR CARRYING OUT THE INVENTION

[0029] The explosive composition according to the invention is obtained by using a fuel component and an oxidizer component as an essential component and milling them with an aqueous emulsion of a hydrophobic tackifier and shaping, if necessary, and then drying. The tackifier used in the invention is a hydrophobic tackifier and forms an aqueous emulsion by dispersing into water. As the hydrophobic tackifier are mentioned, for example, a rubber-based tackifier, an acryl-based tackifier and a silicone-based tackifier, but the acryl-based tackifier is preferable from a viewpoint of the burning rate and the cleanability of combustion gas. The amount of the tackifier used is preferable to be 2-15 mass% as a solid content in the explosive composition, and is more preferable to be 3-9 mass% as a solid content from a view point of the shapability and the cleanability of combustion gas. The heat decomposition temperature of the tackifier is desirable to be higher than a self-decomposition temperature of the explosive composition and is preferable to be not lower than 200˚C. Moreover, it is preferable to use the acryl-based tackifier so as to render the explosive composition before the shaping into a glutinous state in view of the extrusion molding.

[0030] As the fuel component used in the invention may be mentioned a nitrogen-containing compound and boron. As the nitrogen-containing compound may be mentioned at least one selected from the group consisting of guanidine, tetrazole, bitetrazole, triazole, hydrazine, triazine, azodicarbonamide, dicyanamide and derivatives thereof and a nitramine compound. More concretely, there may be mentioned 5-oxo-1,2,4-triazole, tetrazole, 5-aminotetrazole, nitric acid aminotetrazole, nitroaminotetrazole, bitetrazole (5,5'-bi-1H-tetrazole), 5,5'-bi-1H-tetrazole diammonium salt, azobistetrazole, 5,5'-azotetrazole diguanidine salt, guanidine, nitroguanidine, cycanoguanidine, triaminoguanidine nitrate, guanidine nitrate, aminoguanidine nitrate, biuret, azodicarbonamide, carbohydrazide, carbohydrazide nitrate complex, oxalic acid hydrazide, hydrazine nitrate complex, anmine complex and so on. Among these nitrogen-containing compounds, one or more selected from the tetrazole derivatives and guanidine derivatives are preferable in view that they are cheap and good in the reactivity and relatively easy in the handling, and particularly one or more selected from nitroguanidine, guanidine nitrate, bitetrazole, azobistetrazole and 5-aminotetrazole are preferable.

[0031] The content of the fuel component (compounding ratio) in the explosive composition according to the invention is preferably about 15-50 mass%, more preferably about 20-45 mass%. When the content of the fuel component (compounding ratio) is less than 15 mass%, there is a tendency that when the explosive composition is used as a gas generating agent, the mole number of the gas generated per 100 g of the explosive composition decreases and the amount of NOx generated increases due to oxygen excess. While, when the content of the fuel component (compounding ratio) exceeds 50 mass%, the fuel component having a low specific gravity becomes large and hence the true specific gravity of the explosive composition as the gas generating agent reduces to decrease the filling amount per volume of the gas generator for an air bag, a sheet belt pretensioner or the like. And also, the oxidizer component is lacking and hence the generation of CO gas tends to be increased. When the nitrogen-containing compound is used together with boron as the fuel component, the ratio of boron used per 1 part by mass of the nitrogen-containing compound is preferably 0.1-10 parts by mass, more preferably 0.5-5 parts by mass.

[0032] As the oxidizer component used in the invention are mentioned, for example, chlorates, perchlorates, nitrates and basic nitrates. The chlorate includes, for example, an alkali metal salt of chloric acid such as potassium chlorate, sodium chlorate or the like; an alkaline earth metal salt of chloric acid such as barium chlorate, calcium chlorate or the like; and an ammonium salt of chloric acid such as ammonium chlorate or the like. The perchlorate includes, for example, an alkali metal salt of perchloric acid such as potassium perchlorate, sodium perchlorate or the like; an alkaline earth metal salt of perchloric acid such as barium perchlorate, calcium perchlorate or the like; and an ammonium salt of perchloric acid such as ammonium perchlorate or the like. The nitrate includes, for example, an ammonium salt of nitric acid such as ammonium nitrate or the like; an alkali metal salt of nitric acid such as sodium nitrate, potassium nitrate or the like; an alkaline earth metal salt of nitric acid such as barium nitrate, strontium nitrate or the like; and so on. As the basic nitrate are mentioned, for example, basic copper nitrate, basic manganese nitrate, basic iron nitrate, basic molybdenum nitrate, basic bismuth nitrate, basic cerium nitrate and so on. Among them, the perchlorate, nitrate or basic nitrate is preferable. Among the perchlorates is preferable ammonium perchlorate or potassium perchlorate which is large in the amount of the gas generated and high in the reactivity. Among the nitrates is preferable a nitrate of a metal selected from alkali metals and alkaline earth metals from a viewpoint of the reactivity and handling property, and particularly potassium nitrate and strontium nitrate are preferable. Among the basic nitrates is preferable basic copper nitrate which is low in the burning temperature and good in the heat stability.

[0033] The content of the oxidizer component (compounding ratio) in the explosive composition according to the invention is preferably about 40-80 mass%. When the content of the oxidizer component (compounding ratio) is less than 40 mass%, oxygen is lacking and the occurrence of CO gas tends to be increased, while when it exceeds 80 mass%, there is a tendency of increasing the amount of NOx generated due to oxygen excess.

[0034] Further, the explosive composition according to the invention may contain metallic powder, a silicon nitride or a metal nitride for increasing the burning rate and more improving the ignition characteristic. As the metallic powder are mentioned, for example, aluminum, magnesium, magnarium, titanium, zirconium and the like. As the silicon nitride or metal nitride are mentioned, for example, silicon nitride, boron nitride, aluminum nitride, magnesium nitride, molybdenum nitride, tungsten nitride, calcium nitride, barium nitride, strontium nitride, zinc nitride, sodium nitride, copper nitride, titanium nitride, manganese nitride, vanadium nitride, nickel nitride, cobalt nitride, iron nitride, zirconium nitride, chromium nitride, tantalum nitride, niobium nitride, cerium nitrides, scandium nitride, yttrium nitride, germanium nitride and the like. The content of the metallic powder, silicon nitride or metal nitride in the explosive composition is preferable to be 0-10 mass%.

[0035] In the explosive composition according to the invention may be further included a surfactant for increasing the milling property of the fuel component, oxidizer component and hydrophobic tackifier and more enhancing the extrusion moldability. As the surfactant may be used any of nonion surfactants, anion surfactants and cation surfactants, but the nonion surfactant such as NOIGEN (made by Dai-ichi Kogyo Seiyaku Co., Ltd.) or the like is desirable. In the nonion surfactant, HLB (Hydrophile Lipophile Balance) value is preferable to be not more than 15. More preferably, it is 3-15. In case of using two or more surfactants, the HLB value is calculated on weighted mean. When the HLB value is too low, the dispersing ability in water system is poor, while when it is too high, the moisture absorption resistance of the explosive composition lowers. The content of the surfactant in the explosive composition is preferably 0-5 mass%.

[0036] In the explosive composition according to the invention may be further included an extrusion assistant as a water retaining agent-lubricant for improving the extrusion property. As the extrusion assistant are mentioned carboxymethyl cellulose (CMC), sodium salt of carboxymethyl cellulose (CMCNa), potassium salt of carboxymethyl cellulose, ammonium salt of carboxymethyl cellulose, cellulose acetate, cellulose acetate butyrate (CAB), methylcellulose (MC), ethylcellulose (EC), hydroxypropyl methylcellulose (HPMC), hydroxyethylcellulose (HEC), ethylhydroxy ethylcellulose (EHEC), hydroxypropylcellulose (HPC), carboxymethylethyl cellulose (CMEC) and the like. The content of the extrusion assistant is preferable to be 0-1 mass% in the explosive composition.

[0037] A slug-forming agent such as acid clay, kaolin or the like, a chlorine-neutralizing agent such as an alkali metal, an alkaline earth metal or the like, a burning catalyst such as molybdenum oxide, vanadium oxide, iron oxide, copper oxide, chromium oxide, cobalt oxide, aluminum oxide or the like, and so on may be compounded, if necessary.

[0038] The explosive composition according to the invention is preferable to be used as a shaped body. The shaped body of the explosive composition can be used as a gas generating agent, an autoignition agent or an enhancer agent. In case of the gas generating agent, it is preferable to use the nitrogen-containing compound as the fuel. The enhancer agent is used for enlarging a flame produced from an exploder to easily burn the gas generating agent, in which the nitrogen-containing compound or boron is preferable as the fuel. The autoignition agent has a nature of self-igniting at a temperature lower than the ignition temperature of the gas generating agent such as about 180˚C, and the use of 5-aminotetrazole, alkali metal salt of nitric acid or molybdenum trioxide is mentioned (see JP-A-2001-80986).

[0039] Also, the explosive composition shaped body according to the invention is used, for example, in parts for automobile safety device. As the part for automobile safety device are mentioned, for example, a gas generator for an air bag, a gas generator for a sheet belt pretensioner, and a small-size gas generator for a bonnet lifting device. The explosive composition shaped body according to the invention is used in these gas generators in combination with the gas generating agent, autoignition agent and enhancer agent, if necessary.

[0040] The explosive composition shaped body according to the invention takes on a powdery or granular form. As the form of the shaped body are mentioned an extrusion molded body and a tablet. As the form of the extrusion molded body are mentioned a granular form, a columnar form, a cylindrical form, a prismatic form, a porous cylindrical form, a porous prismatic form and the like. As the tablet are mentioned a tablet pellet and the like.

[0041] The explosive composition according to the invention is produced by milling and drying the fuel component and the oxidizer component with the aqueous emulsion of the hydrophobic tackifier. At this moment, the aforementioned metallic powder, silicon nitride, metal nitride, surfactant, extrusion assistant, burning catalyst and the like may be properly selected and compounded within a range not damaging the object of the invention in addition to the above components. Also, in the production of the explosive composition shaped body according to the invention, the fuel component and the oxidizer component may be milled with the aqueous emulsion of the hydrophobic tackifier and shaped and then dried and solidified. In this case, it is preferable that the milled mass obtained by milling the components is shaped in a shaping machine, and also the mixing and milling may be carried out in the shaping machine, particularly an extruder. As the shaping machine are mentioned, for example, a tableting machine, a compression shaping machine, an extrusion molding machine, a swaging machine, a granulating machine and the like. Among them, the extrusion molding machine is preferable.

<<EXAMPLES>>

[0042] The invention will be further described in detail with reference to examples, but the invention is not limited to the following examples.

(Example 1)

[0043] In a rocking mixer are mixed 40 mass% of guanidine nitrate, 25 mass% of strontium nitrate and 25 mass% of basic copper nitrate, which are then mixed with 9 mass% as a solid content of an aqueous emulsion of an acryl-based tackifier and 1 mass% of a surfactant, NOIGEN TDS-30 (made by Dai-ichi Kogyo Seiyaku Co., Ltd.) having an HLB value of 8.0 in a milling machine and further 15 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 2.5 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 6.5 mm, which is dried to obtain an explosive composition shaped body for a columnar gas generating agent.

[0044] In the resulting explosive composition shaped body for the gas generating agent, a burning rate (40%-70%) dp/dt as a parameter indicating the ignitability and combustibility is 2.32 MPa/ms. The burning rate (40%-70%) dp/dt means a gradient of a curve arriving from 40% to 70% when a maximum pressure is 100% as determined from a combustion curve between burning time and burning pressure by measuring a pressure inside a bomb through a pressure sensor when 0.3 g of an enhancer agent and 2.5 g of a gas generating agent are burnt in the bomb of 18 cc.

(Example 2)

[0045] In a rocking mixer are mixed 40 mass% of guanidine nitrate, 25 mass% of strontium nitrate, 25 mass% of basic copper nitrate and 1 mass% of hydroxypropyl methylcellulose, which are then mixed with 8 mass% as a solid content of an aqueous emulsion of an acryl-based tackifier in a milling machine and further 15 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 2.5 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 6.5 mm, which is dried to obtain an explosive composition shaped body for a columnar gas generating agent.

[0046] In the resulting explosive composition shaped body for the gas generating agent, a burning rate (40%-70%) dp/dt as a parameter indicating the ignitability and combustibility is 2.27 MPa/ms. The burning rate (40%-70%) dp/dt means a gradient of a curve arriving from 40% to 70% when a maximum pressure is 100% as determined from a combustion curve between burning time and burning pressure by measuring a pressure inside a bomb through a pressure sensor when 0.3 g of an enhancer agent and 2.5 g of a gas generating agent are burnt in the bomb of 18 cc.

(Example 3)

[0047] In a rocking mixer are mixed 10 mass% of 5-aminotetrazole and 68 mass% of potassium nitrate, which are then mixed with 12 mass% of boron, 9 mass% as a solid content of an aqueous emulsion of an acryl-based tackifier and 1 mass% of a surfactant, NOIGEN TDS-30 (made by Dai-ichi Kogyo Seiyaku Co., Ltd.) in a milling machine and further 16 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 1.8 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 2.5 mm, which is dried to obtain an explosive composition shaped body for a columnar gas generating agent.
[0048] In the resulting explosive composition shaped body for the gas generating agent, a burning rate (30%-70%) dp/dt as a parameter indicating the ignitability and combustibility is 10.3 MPa/ms. The burning rate (30%-70%) dp/dt means a gradient of a curve arriving from 40% to 70% when a maximum pressure is 100% as determined from a combustion curve between burning time and burning pressure by measuring a pressure inside a bomb through a pressure sensor when 0.3 g of an enhancer agent and 2.5 g of a gas generating agent are burnt in the bomb of 18 cc.

(Example 4)

[0049] In a rocking mixer are mixed 26 mass% of ammonium perchlorate, 26 mass% of strontium nitrate and 4 mass% of copper oxide as a burning catalyst, which are then mixed with 34 mass% of nitroguanidine, 9 mass% as a solid content of an aqueous emulsion of an acryl-based tackifier and 1 mass% of a surfactant, NOIGEN TDS-30 (made by Dai-ichi Kogyo Seiyaku Co., Ltd.) in a milling machine and further 13 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 1.5 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 2.0 mm, which is dried to obtain an explosive composition shaped body for a columnar gas generating agent.
[0050] In the resulting explosive composition shaped body for the gas generating agent, a burning rate (30%-70%) dp/dt as a parameter indicating the ignitability and combustibility is 13.1 MPa/ms. The burning rate (30%-70%) dp/dt means a gradient of a curve arriving from 40% to 70% when a maximum pressure is 100% as determined from a combustion curve between burning time and burning pressure by measuring a pressure inside a bomb through a pressure sensor when 1250 mg of the explosive composition for the gas generating agent are burnt in the bomb of 10 cc.

(Example 5)

[0051] In a rocking mixer are mixed 28 mass% of 5-aminotetrazole, 61 mass% of potassium nitrate and 4 mass% of molybdenum trioxide, which are then mixed with 6 mass% as a solid content of an aqueous emulsion of an acryl-based tackifier and 1 mass% of a surfactant, NOIGEN TDS-30 (made by Dai-ichi Kogyo Seiyaku Co., Ltd.) in a milling machine and further 16 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 1.8 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 2.5 mm, which is dried to obtain an explosive composition shaped body for a columnar autoignition agent.
[0052] In order to evaluate the performances of the resulting explosive composition shaped body for the autoignition agent, the ignition time at 200˚C and the decomposition starting temperature through TG-DTA thermobalance/differential thermal analytical instrument are measured. As a result, the ignition time at 200˚C is 2 seconds, and the decomposition starting temperature is 175˚C.

(Example 6)

[0053] A weight reduction ratio of the explosive composition shaped body for the enhancer agent obtained in Example 3 is measured by subjecting to a thermal shock test of repeating a temperature change of from -40˚C to 107˚C by 200 cycles and to a heat-resistant test of leaving at 107˚V for 400 hours, 1500 hours or 3000 hours. Also, an internal pressure of a bomb when 1200 mg of the explosive composition for the enhancer agent is burnt in the bomb of 18 cc is measured to determine a relation between a burning time and a burning pressure (30%-70%)dp/dt before and after the test. The results are shown in Table 1. As seen from the results, there is obtained the explosive composition for the enhancer agent in which the weight reduction ratio in the thermal shock test and the heat-resistant test is small and the change of the burning rate is small and the environmental resistance is good.

[0054]

Table 1

	Before test	107˚, 400 hours	107˚C, 1500 hours	107˚C, 3000 hours	Thermal shock test
Weight reduction ratio (%)	-	0.08	0.13	0.26	0.04
(30%-70%)dp/dt Burning rate MPa/ms	10.3	9.8	8.9	8.3	8.2

(Example 7)

[0055] In a rocking mixer are mixed 40 mass% of guanidine nitrate, 25 mass% of strontium nitrate and 25 mass% of basic copper nitrate, which are then mixed with 9 mass% as a solid content of an aqueous emulsion of an acryl-based tackifier and 1 mass% of a surfactant, NOIGEN TDS-80 (made by Dai-ichi Kogyo Seiyaku Co., Ltd.) having an HLB value of 13.3 in a milling machine and further 15 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 2.5 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 6.5 mm, which is dried to obtain an explosive composition shaped body for a columnar gas generating agent.

(Example 8)

[0056] In a rocking mixer are mixed 40 mass% of guanidine nitrate, 25 mass% of strontium nitrate and 25 mass% of basic copper nitrate, which are then mixed with 9 mass% as a solid content of an aqueous emulsion of an acryl-based tackifier and 1 mass% of a surfactant, NOIGEN TDS-200D (made by Dai-ichi Kogyo Seiyaku Co., Ltd.) having an HLB value of 16.3 in a milling machine and further 15 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 2.5 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 6.5 mm, which is dried to obtain a composition shaped body for a columnar gas generating agent.

(Comparative Example 1)

[0057] In a rocking mixer are mixed 41 mass% of guanidine nitrate, 25 mass% of strontium nitrate, 25 mass% of basic copper nitrate, 6 mass% of hydroxypropyl methylcellulose and 3 mass% of polyvinyl pyrrolidone, and further 15 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 2.5 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 6.5 mm, which is dried to obtain an explosive composition shaped body for a columnar gas generating agent.

[0058] An experiment for moisture absorption is carried out with respect to the explosive compositions for the gas generating agent obtained in Examples 1, 7, and 8 and the composition shaped body for the gas generating agent obtained in Comparative Example 1. In this moisture absorption experiment, the explosive composition shaped body for the gas generating agent is exposed to an atmosphere having a relative humidity of 31%, 52%, 80% or 93% at 25˚C to measure a weight increase every a given time. The results on the weight change ratio to weight before the exposure in the measured atmosphere are shown in Table 2. From these results, it can be seen that when the examples are compared with the comparative example as to the weight change ratio after 48 hours, the moisture absorption is less in the examples because the weight change ratio in the examples is 1.42% at maximum, while that in Comparative Example 1 is 1.530%. Also, when the examples are compared with each other, it can be seen that the moisture absorption in large as the HLB value becomes high because the weight change ratio increases in the order that the HLB value of the nonion surfactant is 8.0 in Example 1, and the HLB value is 13.3 in Example 7 and the HLB value is 16.3 in Example 8.

[0059]

Table 2

Example (Comparative Example)	Relative humidity	Weight change ratio after 12 hours (%)	Weight change ratio after 24 hours (%)	Weight change ratio after 48 hours (%)
Example 1	31%	0.035	0.078	0.144
	52%	0.130	0.199	0.265
	80%	0.198	0.305	0.423
	93%	0.313	0.592	0.681
Example 7	31%	0.038	0.081	0.161
	52%	0.132	0.210	0.305
	80%	0.214	0.370	0.514
	93%	0.350	0.780	0.805
Example 8	31%	0.064	0.166	0.17
	52%	0.161	0.314	0.355
	80%	0.247	0.688	0.83
	93%	0.516	1.19	1.42
Comparative Example 1	31%	0.054	0.158	0.180
	52%	0.145	0.291	0.390
	80%	0.230	0.508	0.860
	91%	0.479	0.718	1.530

(Comparative Example 2)

[0060] In a rocking mixer are mixed 26 mass% of ammonium perchlorate, 26 mass% of strontium nitrate, and 4 mass% of copper oxide, 6 mass% of hydroxypropyl methylcellulose and 3 mass% of polyacrylamide as a burning catalyst, which are mixed with 35 mass% of nitroguanidine in a milling machine and further 15 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 1.5 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 2.0 mm, which is dried to obtain a composition shaped body for a columnar gas generating agent.

(Comparative Example 3)

[0061] In a rocking mixer are mixed 11 mass% of 5-aminotetrazole, 68 mass% of potassium nitrate, 6 mass% of hydroxypropyl methylcellulose and 3 mass% of polyacrylamide, which are mixed with 12 mass% of boron in a milling machine and further 15 parts by mass of a deionized water is added per 100 parts by mass of the above component system to conduct uniform milling. Then, the resulting milled mass is extruded into a predetermined shape through a dice of 1.8 mm in diameter of an extruder under a given pressure. The extrusion molded body of the explosive composition is cut at a length of 2.5 mm, which is dried to obtain a composition shaped body for a columnar enhancer agent.

[0062] The extrusion moldability, fixation between shaped bodies, cleanability of a shaping machine are observed with respect to the explosive composition shaped bodies for the gas generating agent obtained in Examples 1 and 3, the composition shaped bodies for the gas generating agent obtained in Comparative Examples 1 and 2, the explosive composition shaped body for the enhancer agent obtained in Example 4 and the composition shaped body for the enhancer agent obtained in Comparative Example 3 and further the explosive composition shaped body for the gas generating agent obtained in Example 8. The results are shown in Table 3. From these results, when the examples are compared with the comparative examples, all of the examples are good in the extrusion moldability and the cleanability of the shaping machine, and also the fixation between the shaped bodies is not observed. On the contrary, the comparative examples are good in the extrusion moldability, but the cleanability of the shaping machine is bad and the fixation between the shaped bodies is observed. Moreover, each symbol in Table 3 means the following.

[0063]

Extrusion moldability:

○ shaped by the extruder

X not shaped by the extruder

Cleanability of the shaping machine:

○ substances adhered to the extruder can be removed by hand
X substances adhered to the extruder can not be removed by hand, so that they can be first removed by using a scraper after the substances adhered to each part are made at a wet state with hot water.

[0064]

Table 3

Example (comparative Example)	Extrusion moldability	Fixation between shaped bodies	Cleanability of shaping machine
Example 1	○	none	○
Example 3	○	none	○
Example 4	○	none	○
Example 8	○	none	○
Comparative Example 1	○	presence	X
Comparative Example 2	○	presence	X
Comparative Example 3	○	presence	X

Claims

1. An explosive composition **characterized by** milling and drying a fuel component and an oxidizer component in the presence of an aqueous emulsion of a hydrophobic tackifier.

2. The explosive composition according to claim 1, wherein a content of the hydrophobic tackifier is 2-15 mass%.

3. The explosive composition according to claim 1 or 2, wherein the hydrophobic tackifier is at least one selected from the group consisting of a rubber-based tackifier, an acryl-based tackifier and a silicone-based tackifier.

4. The explosive composition according to claim 3, wherein the hydrophobic tackifier is an acryl-based tackifier.

5. The explosive composition according to claim 3 or 4, wherein the hydrophobic tackifier has a heat decomposition temperature of not lower than 200˚C.

6. The explosive composition according to any one of claims 1-5, wherein the fuel component is a nitrogen-containing compound and/or boron.

7. The explosive composition according to claim 6, wherein the nitrogen-containing compound is at least one selected from the group consisting of guanidine, tetrazole, bitetrazole, triazole, hydrazine, triazine, azodicarbonamide, dicyanamide and derivatives thereof and a nitramine compound.

8. The explosive composition according to any one of claims 1-7, wherein the oxidizer component is at least one selected from the group consisting of a chlorate, a perchlorate, a nitrate and a basic nitrate.

9. The explosive composition according to claim 8, wherein the oxidizer component is at least one selected from the

group consisting of ammonium perchlorate, potassium perchlorate, sodium perchlorate, potassium nitrate, sodium nitrate, strontium nitrate and basic copper nitrate.

10. The explosive composition according to any one of claims 1-9, which further contains at least one selected from a metallic powder, silicon nitride and a metal nitride.

11. The explosive composition according to any one of claims 1-10, which further contains a surfactant.

12. The explosive composition according to claim 11, wherein the surfactant is a nonionic surfactant having a HLB value of not more than 15.

13. An explosive composition shaped body **characterized by** milling, shaping and drying a fuel component and an oxidizer component as claimed in any one of claims 1-9 in the presence of an aqueous emulsion of a hydrophobic tackifier.

14. The explosive composition shaped body according to claim 13, wherein the shaped body is any of a gas generating agent, an autoignition agent and an enhancer agent.

15. The explosive composition shaped body according to claim 13 or 14, wherein the shaped body is for an automotive safety device.

16. The explosive shaped body according to any one of claims 13-15, wherein the shaped body has any of a granular form, a tablet form, a columnar form, a cylindrical form, a prismatic form, a porous cylindrical form and a porous prismatic form.

17. The explosive composition shaped body according to any one of claims 13-16, which further contains at least one selected from a metallic powder, silicon nitride and a metal nitride.

18. The explosive composition shaped body according to any one of claims 13-17, which further contains a surfactant.

19. The explosive composition shaped body according to claim 18, wherein the surfactant is a nonionic surfactant having a HLB value of not more than 15.

20. A method of producing an explosive composition, which comprises milling a fuel component and an oxidizer component with an aqueous emulsion of a hydrophobic tackifier and drying them.

21. A method of producing an explosive composition shaped body, which comprises milling a fuel component and an oxidizer component with an aqueous emulsion of a hydrophobic tackifier and shaping, drying and solidifying them.

22. The method of producing an explosive composition shaped body according to claim 21, wherein the shaping is an extrusion molding.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/058339

A. CLASSIFICATION OF SUBJECT MATTER
C06B23/00(2006.01)i, *C06B21/00*(2006.01)i, *C06B29/00*(2006.01)i, *C06B31/00*(2006.01)i, *C06B33/00*(2006.01)i, *C06B43/00*(2006.01)i, *C06B45/00*(2006.01)i, *C06C7/00*(2006.01)i, *C06D5/00*(2006.01)i, *C06D5/06*(2006.01)i,

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C06B21/00-49/00, C06C7/00-9/00, C06D5/00-5/10, B60R21/26-21/30, 21/34, 22/46

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2006	Toroku Jitsuyo Shinan Koho	1994-2007

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2003-112991 A (NOF Corp.), 18 April, 2003 (18.04.03), (Family: none)	1-9,13-16, 20-22 10-12,17-19
Y	JP 10-265290 A (Daicel Chemical Industries, Ltd.), 06 October, 1998 (06.10.98), & CN 1220650 A & DE 69830372 T2 & EP 913375 A1 & KR 2000015965 A & US 6505562 B1 & WO 98/42642 A1	10-12,17-19
Y	JP 2-271987 A (Director General of Technical Research and Development Institute of Defense Agency et al.), 06 November, 1990 (06.11.90), (Family: none)	11-12,18-19

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 05 July, 2007 (05.07.07)	Date of mailing of the international search report 17 July, 2007 (17.07.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/058339

Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

B60R21/26(2006.01)n, *B60R21/34*(2006.01)n, *B60R22/46*(2006.01)n

(According to International Patent Classification (IPC) or to both national classification and IPC)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2000095592 A **[0002] [0003] [0003]**
- JP 2003524565 A **[0002] [0003]**
- JP 2003238285 A **[0002] [0003]**
- JP 2001192288 A **[0002] [0003]**
- JP 2001080986 A **[0038]**