Environmentally Friendly Energetic Materials for Initiation Devices

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Abstract: The problems of synthesis, properties and applications of environmentally-friendly, primary explosives are discussed. Several prospective, lead-free primary explosives have been prepared and thoroughly studied during recent decades. However, the manufacture of modern, ‘green’ energetic materials on an industrial scale for practical applications in civil and military primers, is a task for the near future.

Keywords: lead azide (LA), lead styphnate (LS), low toxicity primary explosives

Introduction

Lead azide (LA), lead styphnate (LS) and mercury fulminate (MF) remained the main primary explosives for civil and military primers and detonators. Even after about a century of extensive research, appropriate replacements for MF having acceptable stability, sensitivity, and performance remain elusive.
Mercury and its compounds are exceedingly toxic towards biological systems and, especially to warm-blooded organisms. Mercury cations readily complex with different proteins. This results in inhibitory effects on a number of enzymes and numerous disorders of key metabolic processes. Mercury compounds also show toxic effects on the nervous system. The chronic effect of mercury salts on warm-blooded organisms results in malfunctioning of the central nervous system, weakness of eye-sight, and vibration of the extremities. Mercury also shows a pronounced toxic effect upon the kidneys. In marine eco-systems mercury cations are readily converted to alkylated forms, \( \text{Hg}^{2+} \rightarrow \text{Hg}(R)^+ \rightarrow \text{Hg}(R)_2 \) which are much more toxic than the initial mercury cations. Such organometallic mercury compounds remain in the organism much longer, in comparison with the mercury salts, and their disposal is a significant problem [1].

At present it is illegal for MF to be used in commercial primers and blasting caps, essentially all over the world, because of its harmful effect on people’s health and ecosystems.

Tons of lead-containing super-toxicants settle in the environment every year as a result of using LA and LS in primers and detonators in industry and for military aims.

Super-ecotoxicants are characterized by a wide range of toxic effects upon ecological systems and warm-blooded organisms. Lead is also treated as a super-ecotoxicant and shows toxic effects toward many life-supporting systems, namely:

1. Blood-producing systems. Anemia is the result of chronic lead intoxication. Extreme treatment of experimental animals with lead compounds results in more than halving of the number of red cells in their blood.
2. Lead and its compounds are also injurious to the central nervous system, especially by destroying human memory. Teenagers and children are especially sensitive to lead intoxication. Children living in areas polluted with lead show much lower success in education.
3. Lead is also deposited in bones, replacing calcium salts. Such replacements lead to osteoporosis. Lead is capable of staying in bones for over 25 years.
4. Lead belongs to the so-called thiolic poisons and actively reacts with the SH-groups of a number of proteins. This effect results in disorganization of many metabolic processes in different organisms.

Lead pollution is especially dangerous for ground-based systems as it is effectively deposited and stored in the soil and propagates through nutrition chains [2].

Researches in the field of the synthesis of ‘green’ energetic materials and their applications as replacements for LS and LA in primers and detonators were expanded according to the President Clinton’s (USA) executive orders in 1993, aiming to reduce or eliminate the procurement of hazardous substances and chemicals for federal needs.

**Environmentally friendly energetic materials**

A search for a suitable lead replacement for LA is a very difficult problem because replacement candidates must have explosive performance comparable with LA, sensitivity to external stimuli comparable with LS and yet meet acceptable health and safety standards. The physical properties, sensitivity and explosive performance of LA and LS are shown in Table 1 [3, 4].

**Table 1.** Physical properties, sensitivity and explosive performance of LA and LS

<table>
<thead>
<tr>
<th></th>
<th>Explosive</th>
<th>Maximum of thermal decomposition (DSC) exo., °C</th>
<th>Impact sensitivity, N m</th>
<th>Friction sensitivity, N</th>
<th>Spark sensitivity, mJ</th>
<th>Crystal density, g/cm³</th>
<th>Detonation velocity $D_v$, km/s</th>
<th>Initiating ability (min. charge in a No 8 detonator for Tetryl), g</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA</td>
<td>315</td>
<td>2.5 - 4</td>
<td>0.1</td>
<td>4.7</td>
<td>4.7</td>
<td>5.3</td>
<td>0.025</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>LS</td>
<td>282</td>
<td>2.5 - 5</td>
<td>0.1</td>
<td>0.2</td>
<td>3.1</td>
<td>5.2</td>
<td>&gt;0.5</td>
<td></td>
</tr>
</tbody>
</table>

LA has a threshold of thermal stability of ~200 °C. Charges of LA in primers retain their explosive properties after exposure for 6 h at this temperature. The threshold of thermal stability of LS is close to 150 °C. The initiating ability of LA and LS was tested in a cartridge-case from a No 8 blasting cap. The setup for testing the initiation ability of primary explosives is given in Figure 1. A thermal
pulse initiated the explosion of the primary explosive charge in the blasting cap.

![Figure 1. The setup for testing the initiation ability of primary explosives.](image)

1 – cartridge-case from No 8 blasting cap, d = 6.5 mm; 2 – charge of primary explosive; 3 – charge of a high explosive (HE).

Researchers at Los Alamos National Laboratory (LANL) elaborated and published in 2006 the requirements for ‘green’ replacements of LA and LS in primers and blasting caps [5]. They suggested that lead replacements must retain their energetic properties upon exposure to the atmosphere and must conform to six ‘green’ primary criteria, namely:

1. Insensitivity to moisture and light;
2. Sensitivity to initiation but not too sensitive to handle and transport;
3. Thermally stable to at least 200 °C;
4. Chemically stable for extended periods;
5. Devoid of toxic metals such as lead, mercury and some others;
6. Free of perchlorate which may act as a teratogen and has adverse effects on the function of the thyroid gland.

The existing primary explosives include organic compounds, simple inorganic salts, coordination complexes, and metastable interstitial composites (MICs).

**Nano-scale thermite materials**

Nano-scale thermite materials or metastable intermolecular composites (MICs) composed of nano aluminium and nano oxides of d-metals have high thermal stability. Their interaction corresponds to the following equation:

\[
\text{Al} + \text{Metal Oxide} \rightarrow \text{Al}_2\text{O}_3 + \text{Metal} \\
\rightarrow \text{MICs}
\]
The combustion velocity of some MICs is very high. For example, the nanothermite CuO/Al has a combustion velocity of ~2400 m/s. This high combustion velocity is in the range of explosive velocities, so the CuO/Al nanothermite may have application as a primary explosive [6c]. The sensitivity of MICs to external stimuli provides the possibility for these compositions to be used in primers. However metastable interstitial composites are undesirable for this application because of air oxidation of the aluminum nano particles [4, 6, 7]. In addition the manufacture of MICs is hazardous. Hence MICs do not comply with requirements 1, 2, and 4 of the LANL’s criteria for ‘green’ energetic materials.

Organic compounds

The commercial primary explosive tetracene (1-(5-tetrazolyl)-3-guanyltetracene hydrate, 1) is an environmentally friendly, energetic material because it does not contain any heavy metal or perchlorate ions.

![Tetracene (1)](image)

It is now generally accepted that 1 has a zwitterionic structure. Compound 1 has crystal density ~1.63 g/cm³, and detonation velocity ~5300 m/s. The sensitivity of 1 to impact and to pricking with a steel needle is higher than that of LA or LS to these stimuli. In practice it is used in impact primers and in prick blasting caps as an additive to LS and LA. The temperature of ignition of tetracene 1 is ~160 °C, and the temperature of the onset of intense decomposition is about 140 °C. In the priming ability test the minimal charge of 1 in a No 8 detonator towards PETN was 0.25 g. Compound 1 looses its initiation ability in a No 8 blasting cap on being compressed under pressures exceeding 15 MPa. Tetracene slowly decomposes above 60 °C, decomposes completely at 90 °C during 6 days and is destroyed by wet CO₂ [2]. Hence tetracene 1 does not meet requirements 1 and 3 of the LANL’s criteria for ‘green’ energetic materials.

Reaction of 1 with sodium nitrite in aqueous acidic media at 70 °C affords a new energetic compound (iso-DTET, 2) with a high sensitivity to mechanical stimuli. The most probable structure of compound 2 corresponds to 5-tetrazoloazo-1’-tetrazole-5’-amine,
The onset temperature for intensive thermal decomposition of 2 is about 214 °C (DSC), its sensitivity to impact is 0.016 J (compound 1 - 0.021 J), its sensitivity to friction is 800 g (compound 1 – 1100 g), and its sensitivity to spark is ~3.30 mJ (compound 1, >7.43 mJ) [8]. The prospects for the practical application of iso-DTET (2) in any ‘green’ initiation devices will become clearer after further tests.

The primary explosive 2-diazoio-4,6-dinitro-1-phenolate (DDNP, 3) also may be considered as an environmentally friendly, energetic material.

It is argued that compound 3 exists in the solid state either as an open phenolic structure or as a cyclic benzoxadiazole structure [3]. Quantum-chemical calculations of the structure of compound 3 at the density functional theory level (computed [MPW1PW91/6-31G(d, p)]) and the experimental X-ray structural parameters of DDNP show it as the open-ring structure given below [9]:
The agreement between the measured and the computed structural parameters is very good.

DDNP (3) has crystal density \(\sim 1.71 \text{ g/cm}^3\), and a detonation velocity of \(\sim 6900 \text{ m/s} \) (at a density of 1.6 g/cm\(^3\)). Its temperature of ignition is \(\sim 172 \degree C\). The brisance of compound 3 is about 95\% of that for TNT [3]. The initiation ability of compound 3 is less than that of LA. Unfortunately, this primary explosive is not stable upon exposure to light.

DDNP (3) is prepared by diazotization of picraminic acid with sodium nitrite in an acidic medium. This method is unacceptable from environmental considerations because a lot of toxic acid waste has to either be disposed of or utilized. In addition, compound 3 activates an inappropriate immune system response that predisposes towards allergic syndromes; hence personnel are at serious health risk.

DDNP (3) is used as a replacement of LA in industrial blasting caps in China and as a replacement of LS in a nontoxic SINTOX stab mix (in admixture with tetracene, zinc peroxide, and titanium) or its analogues in commercial impact primers in West European countries and the USA [5, 10]. In all, DDNP (3) does not meet requirements 1 and 3 of the LANL’s criteria for ‘green’ energetic materials.

1,3,5-Triazido-2,4,6-triazine (TAT, 4) or cyanuric triazide is a low toxicity, environmentally friendly, organic primary explosive [2]. The melting point of 4 is \(\sim 94 \degree C\). TAT (4) has crystal density \(\sim 1.73 \text{ g/cm}^3\), detonation velocity \(\sim 7300 \text{ m/s} \) (at a density of 1.5 g/cm\(^3\)), and sensitivity to spark 1.2 mJ. The temperature of ignition of compound 4 is \(\sim 205 \degree C\). The gaseous detonation products of 4 are non-toxic. TAT is a more effective primary explosive than LA. The minimal charge of compound 4 in a No 8 detonator in the priming ability test towards
Tetryl was 0.02 g. Compatibility tests carried out by means of differential scanning calorimetry (DSC) show that TAT (4) is compatible with aluminum and stainless steel as well as with energetic nitramines including RDX, HMX and CL-20. Compound 4 loses its initiation ability in a No 8 blasting cap on being compressed under pressures exceeding 20 MPa.

![1,3,5-Triazido-2,4,6-triazine (4)](image)

The replacement of LA and LS used in the initiation charge of NOL-130 stab mix (antimony sulfide, barium nitrate, LA, LS basic, tetracene) by TAT (4) was studied. For this purpose, TAT (4) was blended, by means of a physical mixing process, with antimony sulfide, barium nitrate and tetracene to furnish a new formulation named NOL-130 Green (NOL-130G). According to the testing results, replacing the standard NOL-130 with the TAT-based mixture resulted in a successfully functioning stab M55 detonator, which also produced the required dent depth [11].

TAT (4) is a volatile organic substance. It begins to sublime above 30 °C. Compound 4 is decomposed by hot water and on heating above 100 °C in the solid state. Hence TAT (4) does not meet requirements 1 and 3 of the LANL’s criteria for ‘green’ energetic materials.

2,4-Dinitrophenyldiazonium perchlorate (DPDP, 5) was recommended as an environmentally friendly, primary explosive for application in commercial detonators [12, 13].

![2,4-Dinitrophenyldiazonium perchlorate (5)](image)

DPDP (5) is a more effective primary explosive than LA. In a priming ability test the minimal charge of compound 5 in a No 8 detonator towards Tetryl was
0.007 g. The temperature of ignition of compound 5 is ~218 °C. Unfortunately, compound 5 is hygroscopic and loses its initiation ability in a No 8 blasting cap after being exposed to a humid atmosphere. In addition, the molecule of 5 contains the toxic perchlorate anion [4b]. Hence, DPDP (5) does not meet requirements 1, 3 and 6 of the LANL’s criteria for ‘green’ energetic materials.

Simple inorganic salts

Potassium 4,6-dinitro-7-hydro-7-hydroxybenzfuroxanide (KDNBF, 6) is a low-toxicity, environmentally friendly, energetic compound [14, 15].

![Potassium 4,6-dinitro-7-hydro-7-hydroxybenzfuroxanide (6)](image)

Compound 6 has a crystal density of ~2.21 g/cm³. The sensitivity of KDNBF (6) to impact and friction is the same as the sensitivity of LS to these stimuli. The temperature of ignition of 6 is ~210 °C, the temperature of the onset of intensive decomposition is about 190 °C. KDNBF (6) has an initiation ability less than that of MF. It was used in low toxicity mixtures with the environmentally friendly oxidizer KNO₃ and sensitizing additives for primers’ production in the USA. The manufacture of 6 was organized in the USA after World War II. KDNBF is a really ‘green’ explosive but it does not meet requirement 3 of the LANL’s criterion for ‘green’ energetic materials.

Recently the potassium salt of 4,6-dinitro-7-hydroxybenzofuroxan (KDNP, 7), a more stable salt compared to compound 6, was prepared and studied as a ‘green’ replacement for LS. The synthesis of KDNP is based on KDNBF (6) as the starting material and it has a similar structure to compound 6 except that it represents a true salt, whereas compound 6 is a Jackson-Meisenheimer adduct.
Potassium salt of 4,6-dinitro-7-hydroxybenzofuroxan (7)

The temperature of the onset of intensive decomposition of compound 7 is about 270 °C (DSC) [16]. KDNP (7) is a fast deflagrating material with good thermal stability and safe handling characteristics. It was approved as safe and suitable for service use and was recommended for USA weapons improvement in February 2009.

Salts of the energetic 5-nitrotetrazole (HNT) belong to a promising class of low toxicity, environmentally friendly, primary explosives for application in commercial primers and blasting caps.

5-Nitrotetrazole, HNT

HNT is a strong NH-acid (pK_a = -0.82) and a weak base (pK_BH⁺ = -9.3). It has an enthalpy of formation, ΔH_f, of 2273 kJ/kg and a detonation velocity (at density of 1.73 g/cm³) of ~8.9 km/s [17]. The explosive properties of many stable HNT metal salts were investigated before World War II [17]. In the course of a search for low toxic, environmentally friendly, primary explosives some HNT metal salts were reinvestigated recently.

The potassium (8), rubidium (9) and cesium (10) salts of 5-nitrotetrazole were prepared and thoroughly studied as potentially ‘green’ primary explosives [18]. Some properties of the salts are shown in Table 2.
Salts 8-10 exhibit the properties of primary explosives and have sensitivities to both impact and friction similar to technical grade LA (impact = 3.0-6.5 J and friction = 0.1-1.0 N). It was shown that salts 8-10 have initiation ability in a No 8 blasting cap and can be qualified as ‘green’ primary explosives. Unfortunately, the temperatures of decomposition of these salts do not exceed ~195 °C and therefore do not meet requirement 3 of the LANL’s criterion for ‘green’ energetic materials.

The copper (II) salt of 5-nitrotetrazole 11 is a primary explosive with high initiation ability, approximately the same as LA. Bis-(5-nitrotetrazolato)copper (II) (Cu(NT)2, 11) has a crystal density of ~2.11 g/cm³, and the temperature of the onset of intensive decomposition is about 278 °C [19, 20].

Salt 11 was recommended as a prospective, environmentally friendly, primary explosive for primers and detonators. The pilot plant technology of copper salt 11 preparation has been worked out in the USA. The prospects for practical application of Cu(NT)2 (11) in ‘green’ initiation devices should become clearer after a further tests.

Notwithstanding that copper belongs to the so-called biometals, in high concentrations it is rather toxic towards the majority of organisms and ecological systems. High concentrations of copper stimulate the production of active oxygen species that result in the oxidative damage of proteins and nucleic acids. However a lack of copper also leads to the inactivation of the main antioxidant enzymes and initiates disorders in the energetic processes in living organisms. Consequently, in ecological systems the optimum concentration of copper should be maintained because it is necessary for the normal functioning of all the organisms in the global ecological system [21].

Substitution of lead and mercury for copper in primary explosives is a modern trend in the manufacture of less hazardous explosives and may be considered as the first step to the so-called ‘green’ primary explosives.
Another low-toxicity LA replacement is the copper (I) salt of 5-nitrotetrazole ($\text{Cu}_2(\text{NT})_2$, DBX-1, 12).

![Copper (I) salt of 5-nitrotetrazole, DBX-1 (12)](image)

Compound 12 has a crystal density of ~2.59 g/cm$^3$, a detonation velocity of ~7000 m/s and sensitivity to spark of 3.1 mJ. The heat of explosion of salt 12 is 3816.6 J/g; the heat of formation is 280.9 J/g. The particle size of copper salt 12 crystals is 10-40 μm. The sensitivity of compound 12 to impact, friction and spark is nearly the same as that for LA (Table 3).

**Table 3.** Physical properties, sensitivity and explosive performance of DBX-1 (12) [22].

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Maximum of thermal decomposition (DSC) exo., °C</th>
<th>Impact sensitivity, J</th>
<th>Friction sensitivity, N</th>
<th>Spark sensitivity, mJ</th>
<th>Crystal density, g/cm$^3$</th>
<th>Detonation velocity $D_\text{p}$, km/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBX-1, (12)</td>
<td>333</td>
<td>0.036</td>
<td>0.1</td>
<td>3.1</td>
<td>2.58</td>
<td>~7.0</td>
</tr>
<tr>
<td>LA</td>
<td>315</td>
<td>0.089</td>
<td>0.1</td>
<td>4.7</td>
<td>4.7</td>
<td>5.3</td>
</tr>
</tbody>
</table>

The temperature of the onset of intensive decomposition of copper salt 12 is about 333 °C (DSC). The ignition temperature for a 1-s delay is 356 °C, and for a 5-s delay is 351 °C. The weight loss of DBX-1 after 24 h exposure at 181 °C was 0% (for LA the weight loss was 14.57% under the same conditions). DBX-1, like LA, is not subjected to overpressing. In the priming ability test the minimal
charge of compound 12 in a model detonator towards RDX was 0.025 g. DBX-1 demonstrated good compatibility with RDX, HMX, CL-20, HNS and some others HEs, as well as with common construction materials.

The tests performed showed that compound 12 could replace LA both in transfer charges and in the NOL-130 stab mixture for the M55 stab detonator (Figure 2).

**Figure 2.** M55 stab detonator.

The testing results demonstrated an acceptable dent depth. The pilot plant technology of copper salt 12 preparation has been worked out in the USA [8, 23-25].

Bis(1-methyl-5-nitraminotetrazolate)copper(II) (13) was suggested as a low toxicity explosive for initiation devices [24, 26].

![Chemical structure of Bis(1-methyl-5-nitraminotetrazolate)copper(II) (13)](image)

The sensitivity to impact and friction of 13 is the same as for primary
explosives. The temperature of the onset of intensive decomposition of 13 is about 252 °C (DSC). It was shown experimentally that the exposure of 13 to 190 °C during 48 h does not change its properties. We conclude that bis(1-methyl-5-nitraminotetrazolate)copper(II) (13) has good thermal characteristics and could be used in ‘green’ primary devices because it meets the requirements of the LANL’s criteria for ‘green’ energetic materials. Further detailed investigations of the properties of copper salt 13 and appropriate tests will allow fields for its practical application to be found.

**Metal complex salts**

By the end of the 20th century many energetic complex salts of d-metals having the general formula $\text{M}_x(\text{L})_y(\text{An})_z$, where $\text{M}$ is the cation of a d-metal, $\text{L}$ is a ligand, $\text{An}$ is an acidic anion, and $x$, $y$, $z$ are stoichiometric coefficients, had been synthesized and investigated as potentially safe and environmentally friendly replacements for the traditional primary explosives LA and LS. The flexible chemical design of energetic complex salts allows a wide variation in their physico-chemical, energetic properties and performance to be obtained. A number of prospective energetic complexes with good initiation ability have been synthesized over recent decades. These are more environmentally friendly than LA and LS and have better safety than industrial primary explosives.

Complex perchlorates of cobalt (III) ammines with tetrazole derivatives as ligands do not contain super-ecotoxic heavy metals in their structure. It was shown that complex salts of ammine cobalt (III) are low toxicity compounds [5]. These complexes are safer than classical primary explosives such as LA or LS. They are not hygroscopic and have sufficiently high thermal stability. Their initiation ability is sufficient for the application of these complexes as primary explosives in safe blasting caps. It is well known that cobalt (III) complex perchlorates such as pentaammine(5-cyanotetrazolato-N$^2$)cobalt (III) perchlorate (CP, 14), pentaammine(5-nitrotetrazolato-N$^2$)cobalt (III) perchlorate (NCP, 15), and tetraammine-bis-(5-nitrotetrazolato-N$^2$)cobalt (III) perchlorate (BNCP, 16) are widely used in safe commercial detonators [27-29].

![Chemical structures of CP, NCP, and BNCP](image-url)
Complex CP was suggested as a lead-free explosive for safe, low-voltage, electric blasting caps. However, the toxic properties of cobalt complex CP (14) forced the USA to cease commercial manufacture of this compound [30]. Some physico-chemical properties of the ammine complexes 15 and 16 are given in Table 4 [3].

### Table 4. Properties of complexes 15 and 16

<table>
<thead>
<tr>
<th>Complex</th>
<th>Crystal density $\rho_{\text{exp.}}$, g/cm$^3$</th>
<th>Detonation velocity, $D_{\text{exp.}}$, km/s</th>
<th>Initiation ability (minimal charge on a No 8 detonator towards RDX), g</th>
<th>Onset of decomposition, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCP, (15)</td>
<td>2.03</td>
<td>6.30 (1.61)</td>
<td>0.15-0.20</td>
<td>265 (DTA/TG)</td>
</tr>
<tr>
<td>BNCP, (16)</td>
<td>2.03</td>
<td>7.12 (1.79) [28]</td>
<td>0.05</td>
<td>269 (DSC)</td>
</tr>
</tbody>
</table>

Complex 15 was tested at the Moscow branch of “Geophysics” corporation (Russia) as the main energetic component of a transformer of the explosive process in the explosion device for use in deep gas and oil boreholes [3]. The tests showed that the transformer of the explosive process did not deteriorate in its performance after exposure during 6 h at 150 °C and the pressure of the bore-hole’s liquids ~80 MPa.

The data of Table 4 demonstrate that complex 16 has a higher initiating ability than complex 15. Complex 16 has a time of deflagration-to-detonation transition (DDT) of ~10 µs, and the heat of decomposition is 3319 J/g (DSC). Complex 16 is more sensitive to mechanical stimuli than complexes 14 and 15, although its sensitivity to impact does not exceed that of modern high explosives. For example, BNCP (16) had sensitivity to impact equal to 8% according to the drop-hammer K-44-2 test (Russian standard GOST 4545-88, mass of the hammer 2 kg); PETN had higher sensitivity to impact (12%) under the same conditions. BNCP (16) was often used as a primary or secondary explosive charge in blasting caps [27]. Complex 16 was also used in the pyrotechnic, automatic control systems of rocket complexes in the USA. Complexes 14-16 and their analogues contain highly toxic perchlorate anions, hence they do not meet requirement 6 of the LANL’s criterion for ‘green’ energetic materials.

It has been found that cobalt (III) ammine coordination complex cations
are not toxic. Replacement of the perchlorate anions in cobalt (III) ammine coordination compounds with anionic tetrazole derivatives as ligands, in order to diminish the toxicity of the energetic anion, reduces the toxic properties of the metal complexes and retains their initiation ability. Such an assumption was proved experimentally using the anions of dinitroguanidine (DNG, 17) and azide [31, 32].

\[
\begin{align*}
\text{NNO}_2 \\
\text{NH}_2 - \text{C} - \text{NH}_2 \text{NO}_2
\end{align*}
\]

\textbf{1,2-Dinitroguanidine (17)}

DNG (17) has an enthalpy of formation of \( \sim 0 \) kJ/mol. The oxygen coefficient (\( \alpha \)) is 1.14 for the neutral molecule of 17 and 1.33 for its anion [33, 34]. Replacement of the anions in the perchlorate ammine complexes 15 and pentaammine[3-nitrofurazan-4-(5'-tetrazolato-N\(^2\'))]cobalt (III) perchlorate (18) was performed. Some physico-chemical and explosive properties of the perchlorate complex 18 are given in Table 5.

![Diagram](attachment:image.png)

\textbf{Pentaammine [3-nitrofurazan-4-(5'-tetrazolato-N\(^2\'))]cobalt (III) perchlorate (18)}

<table>
<thead>
<tr>
<th>Complex</th>
<th>Crystal density ( \rho_{\text{exp.}} ), g/cm(^3)</th>
<th>Detonation velocity ( D_{(p)} ) calc. km/s [35]</th>
<th>Initiation ability (minimal charge in a No 8 detonator towards RDX), g</th>
<th>Peak decomposition, °C, (DTA/TG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>1.97</td>
<td>7.76 (1.97)</td>
<td>0.20</td>
<td>280</td>
</tr>
</tbody>
</table>

The replacement of perchlorate anions by DNG anions in complex 15 was performed according to the Scheme below.
The same method was used for the preparation of complex 20:

Complex 21 was prepared by mixing complex 18 and sodium azide in an aqueous solution:

Some physico-chemical and explosive properties of complexes 19-21 are given in Table 6.
Table 6. Properties of complexes 19-21

<table>
<thead>
<tr>
<th>Complex</th>
<th>Crystal density $\rho_{\text{calc.}}, \text{g/cm}^3$ [35]</th>
<th>Detonation velocity, $D_{\text{p}}(\rho)\text{exp.}, \text{km/s}$</th>
<th>Initiation ability (minimal charge in a No 8 detonator towards RDX), g</th>
<th>Peak decomposition, $^\circ\text{C}$, (DTA/TG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>1.83</td>
<td>6.42 (1.736)</td>
<td>&gt;0.5</td>
<td>185</td>
</tr>
<tr>
<td>20</td>
<td>1.98</td>
<td>6.50 (1.38)</td>
<td>0.48</td>
<td>200</td>
</tr>
<tr>
<td>21</td>
<td>1.95</td>
<td>-</td>
<td>&gt;0.5</td>
<td>165</td>
</tr>
</tbody>
</table>

Studies of complexes 19-21 show that the substitution of perchlorate anions in complexes 15 and 18 for DNG and azide anions decreases the temperature of decomposition of the complexes by 80-100 $^\circ\text{C}$ (Table 6). The initiating ability of complexes 19-21 is lower than that of their parent salts. Complexes 19-21 are insensitive to impact according to the drop-hammer K-44-2 test (Russian standard GOST 4545-88, mass of the hammer is 2 kg). Hence, they may be regarded as safer energetic compounds than PETN. Consequently, complexes 19-21 are not effective primary explosives and do not meet requirement 3 of the LANL’s criterion for ‘green’ energetic materials. Furthermore, dermatitis, asthma, dyspnea, respiratory hypersensitivity and diffuse modular fibrosis are potential symptoms after overexposure to metallic cobalt (which is the product of detonation of these cobalt primers) [5].

The results of systematic studies at LANL in the search for ‘green’ primary explosives among metal complexes of HNT were published in 2006 [5]. The researchers synthesized and investigated a range of lead-free metal complexes of the general formula:

$$(\text{Cat})_{1-4}[\text{M}^{II}(\text{NT})_{3-6}(\text{H}_2\text{O})_{3-0}],$$

where Cat = NH$_4$, Na; M = Fe, Cu.

It was found that complexes $\text{Na}_2[\text{Fe}^{III}(\text{NT})_4(\text{H}_2\text{O})_2]$ (22) and $\text{Na}_2[\text{Cu}^{II}(\text{NT})_4(\text{H}_2\text{O})_2]$ (23) had the properties of primary explosives and were safer than LA or LS (Table 7).
Environmentally Friendly Energetic Materials for Initiation Devices

Table 7. Properties of complexes 22 and 23 [5]

<table>
<thead>
<tr>
<th>Explosive</th>
<th>(\rho_{\text{exp.}}) g/cm(^3)</th>
<th>Sensitivity to impact, cm</th>
<th>Sensitivity to friction, g</th>
<th>Sensitivity to spark, J</th>
<th>Onset of decomposition, °C (DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>2.2</td>
<td>12</td>
<td>20</td>
<td>&gt; 0.36</td>
<td>250</td>
</tr>
<tr>
<td>23</td>
<td>2.1</td>
<td>12</td>
<td>40</td>
<td>&gt; 0.36</td>
<td>259</td>
</tr>
<tr>
<td>LA</td>
<td>4.7</td>
<td>10</td>
<td>6</td>
<td>0.0047</td>
<td>315</td>
</tr>
<tr>
<td>LS</td>
<td>3.0</td>
<td>14</td>
<td>40</td>
<td>0.0002</td>
<td>282</td>
</tr>
</tbody>
</table>

The authors [5] believe that copper complexes 22 and 23 and their analogues meet all of the requirements of the LANL’s criteria for ‘green’ energetic materials.

Complexes 22 and 23 explode in primers as DDT primary explosives. It was shown that the performance of compound 23 improves with loading pressure until a maximum is reached, after which the explosive output decreases (the phenomenon of overpressing, or dead pressing) [25]. The overpressing proves the presence of DDT process. M55 stab detonators were used to examine the performance of complexes 22 and 23 as primary explosives. In the complex 23-M55 stab detonator, the whole amount of LA in the transfer charge was replaced by the copper complex. The initiation efficiency and reliability of detonation of complexes 22 and 23, compared with the lead-containing primary explosives in these representative detonators, were measured and confirmed by the “dents on the hardened steel disk” tests (Figure 2). At present no commercial production of complexes 22 or 23 or their analogues has been reported either in the USA or in other countries.

It is well known that complex hydrazinates of nickel (II) with outer sphere anions as oxidizers may have the properties of primary explosives [29]. These complexes, however, have larger minimal charges compared to LA, and their thermal stability is inferior to that of LA. Hence nickel (II) hydrazinate complexes with anion-oxidizers are not considered as promising ingredients for primers, though a pressing demand for lead-free, environmentally friendly, primary explosives forced researchers to revisit this class of energetic metal complexes. The subsequent studies revealed that complex tris-hydrazinenickel (II) nitrate (\(\text{Ni(N}_2\text{H}_4)_3(\text{NO}_3)_2\), 24) was able to replace LA in commercial blasting caps [36-39].

Some properties of complex hydrazine nickel nitrate 24 are shown in Table 8.
The mean diameter of spheroidal crystals of complex nitrate 24 exceeds 80 µm. The density of the pressed charges of complex 24 is 1.55 g/cm³ (under pressure of 20-40 MPa) and ~1.70 g/cm³ (under pressure of 60-80 MPa). Charges of nickel complex 24 are subject to overpressing at pressures above ~60 MPa. The temperature of ignition of complex 24 is ~167 °C (5-s delay). The activation energy of decomposition of nickel complex 24 is ~78 kJ/mol on the basis of DTA/TG data and 89 kJ/mol based on $T_{\text{ignition}}$, these values being lower than the usual values for primary explosives [2]. The pressure of the gaseous explosion products of complex 24 amounts to 105% of the pressure of the gaseous explosion products of equivalent charges of TNT [40].

The non-hygroscopic complex 24 is insoluble in water, alcohol and acetone. Concentrated sulfuric acid ignites the nickel complex 24, whilst it is fully decomposed by 10% aqueous solution of NaOH. However, sunlight or X-ray irradiation do not influence the substance. The contact of complex 24 with Al, Cu, Fe and stainless steel at room temperature for 8 years did not show any signs of reaction.

Compound 24 has sensitivity to impact equal to that of lead azide; the sensitivity to friction and spark is the same as that of AgN₃ [39]. Adding 40% of water to complex 24 results in the loss of both its initiation ability and its sensitivity to the explosion of industrial blasting caps. Complex 24 is sensitive to IR irradiation. It can be ignited by the beam of a pulsed CO₂ laser with an energy density equal to ~12.0 J/cm².

More than 10 million detonators and electric primers filled with 200 mg charges of complex 24 were prepared and tested in China. The experiments demonstrated the reliability of these devices and the possibility of their application in industry and construction. Unfortunately, complex 24 is not a sufficiently thermally stable, primary explosive and does not meet requirement 3 of the LANL’s criterion for ‘green’ energetic materials.

Bis-hydrazinenickel (II) azide ([Ni(N₂H₄)₂(N₃)₂], 25) is the further lead-free candidate for the replacement of LA in primers [40].

Some properties of complex bis-hydrazine nickel azide (25) are presented in Table 9.
The mean size of green colored aggregates of complex 25 crystals is ~80 µm. The temperature of ignition of complex 25 is ~193 °C (5-s delay). The thermal decomposition curve of complex 25 comprises two stages. The activation energy of the first stage of decomposition of complex 25 is ~142.6 kJ/mol, whereas that of the second stage is ~109.2 kJ/mol. The non-hygroscopic complex 25 is insoluble in water, alcohol and ether, and is readily decomposed by both acids and bases. Complex 25 had sensitivity to impact equal to 35% in the drop-hammer test (mass of the hammer 10 kg, height 55 cm), whereas PETN had sensitivity to impact equal to 100% under the same conditions. Hence, complex 25 is a safer compound than nickel complex 24.

Over 100 000 electric primers filled with 110-130 mg of complex 25 were prepared and tested in China. These experiments demonstrated the reliability of these devices and the possibility of their application in mining and the metallurgical industry. However complex 25 does not meet requirement 3 of the LANL's criterion for ‘green’ energetic materials.

Nickel, like copper, also belongs to the group of biometals and is essential for the native activity of some enzymes. According to the International Agency of Cancer investigation, nickel exhibits carcinogenic activity. The concentration of nickel in the environment is rather low but it persists for a long period. Consequently after a prolonged period of commercial use of complexes 24 and 25 their hazardous effects upon living organisms will persist for many years [42].

### Light-sensitive, environmentally-friendly, energetic materials

Currently electrical means of blasting-cap initiation is generally accepted, but devices used for this purpose are inherently susceptible to accidental initiation by external stimuli such as an electrostatic discharge (ESD), electromagnetic interference (EMI) and radio wave irradiation (RI). Pulsed laser initiation of explosives is a promising new method. Pulsed lasers provide a practical means of electrical isolation of energetic materials, thereby eliminating hazards associated with ESD, EMI and RI [43, 44]. Laser initiation systems can be used in civil construction, mining and drilling gas-oil bore-holes [45]. Light sensitive energetic compounds are a basic elements of laser initiation systems.
The direct laser irradiation of low-density explosives through a transparent window results in an explosion. The initiation threshold is decreased when the window facing the explosive charge is coated with a thin layer of metal. Such a cover completely absorbs the high energy of the laser pulse. The high energy of the mono-pulse (Q-switch regime) of an IR laser (Nd-YAG) is absorbed by a thin titanium film (initiation threshold of explosive $\geq 2$ MWt), which results in plasma formation that is driven into the environmentally friendly low-density, finely dispersed PETN (Figure 3). The laser detonator may be used without a titanium film, but the initiation threshold in this case will be somewhat higher.

![Figure 3. Cross-section of a laser EBW detonator. The laser window is coated with a 0.25 µm layer of titanium.](image)

Such a detonator, by analogy with electric detonators of the exploding wire type, is called a “laser explosive bridge-wire (EBW) detonator with an exploding bridge” [46]. The use of finely dispersed PETN having bulk density 0.9 g/cm$^3$ in a laser EBW detonator is more effective than that with a bulk density of 1.0 g/cm$^3$ [47]. The study of the laser detonator showed that the development time of the detonation process in a 1-mm distance exceeds 100-200 ns, which is considerably higher than the time of the shock wave propagation (10-20 ns), which rules out the classic shock mechanism of detonation propagation (shock initiation). The conclusion which was drawn from the above confirms that under the direct laser initiation of PETN, the deflagration-to-detonation transition (DDT) regime is realized. In low-density laser detonators containing BNCP (16) the DDT regime is also realized.

Because only finely dispersed and low-density explosives may be used
in laser EBW detonators, meeting these requirements reduces the sphere of application of such detonators.

Light-sensitive charges of polymer-bonded mixtures of ‘green’ organic primary explosives with optically transparent polymers were shown to have lower thresholds of initiation by Q-switch Nd-laser irradiation than low-density pressed charges of finely dispersed PETN. The finely ground mixtures have sensitivity to mechanical stimuli not higher than the regular HEs PETN or CL-20. Hexamethylenetriperoxidediamine, or 3,4,8,9,12,13-hexaoxa-1,6-diaza-bicyclo-[4,4,4]-tetradecane (HMTD, 26), known as an environmentally safe (‘green’), non-standard, light-sensitive, primary explosive [48-50], was used in the former USSR as a charge in explosive clinches in the 1950s [51].

![Hexamethylenetriperoxidediamine, HMTD (26)](image)

Some properties of peroxide 26 are given in Table 10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal density, $\rho_{\text{exp.}}, \text{g/cm}^3$</th>
<th>Detonation velocity, $D_{(\rho)}\text{exp.}, \text{km/s}$</th>
<th>Initiation ability (minimal charge in a No 8 detonator towards Tetryl), g</th>
<th>Onset of decomposition, °C, DTA/TG</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMTD (26)</td>
<td>1.57</td>
<td>4.51 (0.88) 5.10 (1.10)</td>
<td>0.05</td>
<td>125-140</td>
</tr>
</tbody>
</table>

White orthorhombic crystals of hexamethylenetriperoxidediamine have a bulk density close to 0.66 g/cm$^3$. HMTD is essentially insoluble in water and organic solvents and its hygroscopicity is negligible. It slowly decomposes above 40 °C in the presence of moisture. At room temperature it is hydrolyzed by both acids and bases. HMTD does not react with aqueous solutions of
NaHCO₃, Na₂CO₃ and NH₃. Under storage, both in air and in airtight containers, hexamethylenetetrahydroperoxidiamine is stable for a sufficiently long time. It is also stable on being kept under a layer of water for about 4 weeks at room temperature, but is completely decomposed after 4 months of storage under water. Traces of acids and metal ions slowly decompose charges of HMTD. Hexamethylenetetrahydroperoxidiamine is readily reduced with Zn metal in HCl medium, with aqueous and alcoholic solutions of SnCl₂ and solutions of HBr or HI. Dry HMTD does not react with metals, but in the presence of moisture metals are easily corroded by HMTD. At high temperatures the product sublimes. The heat of explosion of HMTD is 5080 kJ/kg. The ignition temperature of the peroxide is ~200 °C (delay time is near 1 s). Fine crystals of hexamethylenetetrahydroperoxidiamine have a lower sensitivity to mechanical stimuli than LA and MF and can be pressed up to a density of 1.3 g/cm³, but coarse crystals of HMTD explode when being pressed. The threshold of initiation of HMTD charges with the beam of a Q-switch neodymium glass laser (λ = 1.06 µm, τ = 30 ns) is close to 40 mJ/cm². It is difficult to use pure HMTD in optical detonators because it possesses high sensitivity to external stimuli and high corrosive ability. Using an inert polymer matrix solves both problems. The optically transparent, energetic co-polymer of 5-vinyl-2-methyltetrazole (98%) and methacrylic acid (2%) (polymer PVMT) and inert polymethylmethacrylate (organic glass, Plexiglas, PMMA) were used as polymer matrices as described in paper [50].

The dependence of the momentum of the explosion products (J, kPa·s) on the weight (thickness) of the samples (ms, mg/cm²) for HMTD film formulations containing ~10% of PVMT polymer was measured by the ballistic pendulum method. In these experiments the weights of PBX films were varied from 35 to 110 mg/cm². The average energy density of the laser beam at the surface of the charges was twice as high as the threshold of initiation of the PBX films. The experimental results were approximated to a first degree polynomial (see below).

$$J = (0.0153 \pm 0.0011)ms - (0.1203 \pm 0.0090),$$

$$n = 12, \; r = 0.989,$$

where r is the correlation coefficient, n is the number of experimental points. Hence, a planar detonation wave from the PBX films was apparently realized in the study. The experiments showed that after the laser beam initiation, part of the charge of the PBX films burned and added no energy in the pulse of explosion products. Consequently, the DDT mechanism operates in Q-switch laser initiation of detonation of HMTD – polymer PVMT film formulations. HMTD-PMMA
compositions have a lower momentum of explosion products (J) in comparison with that of the corresponding HMTD – polymer PVMT film formulations. In all, the light-sensitive formulations based on HMTD and optically transparent polymers were suggested as environmentally friendly charges for laser initiation systems [52].

In paper [53] the combustion of thin, light-sensitive films composed of mixtures of the environmentally friendly, organic primary explosive DDNP 3 with polymers cellulose triacetate (CTA) and nitrocellulose (NC) as binders, after irradiation by a Q-switch Nd:YAG-laser beam, was investigated.

\[
\left[ C_6H_7O_2(OC-CH_3)_3 \right]^n \left[ C_6H_7O_2(ONO_2)_3 \right]^m \left[ C_6H_7O_2(OH)(ONO_2)_2 \right]^k
\]

**Cellulose triacetate (CTA)**

**Nitrocellulose (NC)**

The binder concentrations in the formulations comprised 10% and 20%, and the thickness of the films was <100 µm, 250 µm, and 750 µm. It was found that the combustion of a DDNP/CTA thin film of 250 µm thickness by pulse laser ablation takes place in three stages:

- in the 1st stage, the laser ablation generates air shock and scatter of fragments of DDNP (3) particles. This stage lasts less than several tens of µs
- in the 2nd stage, the ejected DDNP (3) particles burn in the ambient air and produce an expanding hot flow field; this stage takes several hundred µs
- finally the film body ignites under the action of the hot ambient flow field in more than 5-7 ms after laser irradiation.

The combustion of a DDNP/CTA film takes place under the action of residual heat produced by laser ablation and combustion of explosive particles ejected during ablation. It has been found that the reaction is retarded with increasing CTA concentration and decreasing DDNP (3) content. The rate of combustion of a DDNP/CTA 8:2 film formulation increases with increasing film thickness (at a thickness < 100 µm the combustion rate is less than 0.1 m/s, at a thickness of 750 µm the combustion rate is ~1.4 m/s).

The energy density of a laser beam influences the rate of combustion of a DDNP/CTA film. It was found that a laser beam energy density equal to 30 J/cm² results in a faster combustion than that under an energy density of 15 J/cm². It was also shown that DDNP/NC films may be more combustible than DDNP/CTA films due to the heat released by both the DDNP and NC ingredients. Hence, the burning rate of reactive thin films is a function of the film composition, the laser specific energy and the film thickness.
Unfortunately, light-sensitive, environmentally friendly, organic energetic materials (PETN, HMTD, and DDNP) do not meet requirement 3 of the LANL’s criterion for ‘green’ energetic materials.

Lead-free primary explosives copper (II) 5-chlorotetrazolate (27) and copper (II) 5-bromotetrazolate (28) were investigated as laser-ignitable primary explosives [54]. Some properties of the salts are shown in Table 11.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Onset of decomposition, °C, DSC exo.</th>
<th>Sensitivity to impact, J</th>
<th>Sensitivity to friction, N</th>
<th>Sensitivity to spark, mJ</th>
<th>Crystal density, g/cm³</th>
<th>Initiation ability (min. charge in a No 8 detonator towards Tetryl), g</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>300 &lt;1 &lt;5 25 2.04 [51] 0.10 [51]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>292 &lt;1 &lt;5 20 - 0.12 [54]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results of the tests shown in Table 11 demonstrate that primary explosives 27 and 28 exhibit high thermal stability and high sensitivity to mechanical stimuli. Both compounds 27 and 28 are classified as “very sensitive” according to the UN Recommendations on the Transport of Dangerous Goods.

The ability of small amounts of compounds 27 and 28 to explode under the influence of laser ignition was determined by placing several milligrams of each primary explosive in a thin glass tube illuminated by a 658-nm 200-mW red laser. Both salts exploded immediately upon illumination. The prospects for practical application of salts 27 and 28 in laser initiation devices may be demonstrated by further tests. Apparently, compounds 27 and 28 do not meet requirement 2 of the LANL’s criterion for ‘green’ energetic materials.

Potassium and barium salts of perchlorylamide, K₂NClO₃ (29) and BaNClO₃ (30) are light-sensitive, primary explosives possessing high thermal stability (Table 12) [55].
Salts 29 and 30 are non-hygroscopic products; salt 29 is soluble in water, but salt 30 does not dissolve either in water or in organic solvents. The toxicological properties of these perchlorylamides are still unknown. The sensitivities of salts 29 and 30 to laser beam irradiation (λ = 1060 nm, τ ≈ 25 ns) have been studied. The diameter of the laser beam was around 4 mm. The total energy of the laser pulse was close to 40 mJ. Light-sensitive, explosive film formulations containing ~50 mg/cm² of salts 29 or 30 were prepared and tested (the film formulations contained ~10% of PVMT polymer). The threshold of initiation of salt 29 was shown to be close to 0.1 J/cm², and for salt 30 it was ~5-7 mJ/cm². The experimental error in the initiation threshold was ~20%. The ballistic pendulum was used for measuring the impulse of the explosive films containing light-sensitive salt 30. The average energy density of the laser beam at the surface of the charges was twice as high as the threshold of initiation of the PBX films. The pulse density (J, dyne/cm²) of the explosion products is related to the unit square mass (m, mg/cm²) of the explosive (thickness of the film) through a simple equation:

\[ J = (162.9 ± 10.1)m - (7918 ± 1172), \]

\[ r = 0.985, n = 10, \]

where \( r \) stands for the correlation coefficient, \( n \) is the number of experimental points. The equation shows that a fraction of the explosive charge does not contribute to the registered loading impact. A fraction of the explosive is likely to be consumed in the DDT process. The prospects for practical application of salts 29 and 30 in laser primers will become clearer after further tests.

The complex tris-amminecopper (II) 5-nitrotetrazolate (31) is a lead free, laser ignitable, primary explosive [57].
Some properties of salt 31 are shown in Table 13.

Table 13. Some properties of complex tris-amminecopper (II) 5-nitrotetrazolate (31)

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Onset of decomposition exo., °C (DSC)</th>
<th>Sensitivity to impact, J</th>
<th>Sensitivity to friction, N</th>
<th>Sensitivity to spark (20 kV electrostatic discharge (+/-))</th>
<th>Thermal shock</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>245</td>
<td>&lt;2</td>
<td>&lt;18</td>
<td>-</td>
<td>explodes</td>
</tr>
</tbody>
</table>

Special care must be taken when handling compound 31 as it is an extremely sensitive material. Complex 31 is essentially insoluble in most polar solvents and dissolves only to a low extent in coordinating solvents such as concentrated ammonia or pyridine. It exhibited laser initiation capability. It was initiated by a laser beam of ca. 300 mW power in the course of Raman spectral measurements. The possibilities for practical applications of complex salt 31 in impact or laser primers will become clearer after further tests.

The light-sensitive, lead-free complex copper nitrates with 5,5’-bis-(1H-tetrazolyl)amine 32 and 5,5’-bis-(2-methyl-tetrazolyl)amine 33 as ligands were reported in [58].
Complexes 32 and 33 were shown to have low sensitivity to friction. Complex 32 is more sensitive to impact than complex 33. Evidently, the methyl groups in the molecule of the 5,5′-bis-(2-methyl-tetrazolyl)amine ligand flegmatized complex 33 towards external stimuli. Complexes 32 and 33 were initiated by a Nd:YAG laser beam (λ=1064 nm) with ~100-200 mW power in the course of Raman measurements. The environmentally friendly, copper complex salts 32 and 33 need further investigation before their application as ‘green’ primers can be recommended.

The lead-free, perchlorate copper complex of bis-3(5)-hydrazino-4-amino-1,2,4-triazole as a ligand (34) has a low threshold of initiation (~1.1·10⁻⁵ J) by a Q-switch Nd:YAG-laser beam (λ = 1064 nm, τ = 30 ns, d = 0.48 mm) [59-61].

\[
\text{Cu}
\left[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{NH}_2 \\
\text{N} \\
\text{N} \\
\text{NH}_2
\end{array}
\right] (\text{ClO}_4)_2
\]

(34)

The complex 34 is a hazardous explosive because it has high sensitivity to mechanical stimuli, approaching that of industrial primary explosives such as lead azide or lead styphnate. Complex 34 has a short deflagration-to-detonation (DDT) distance. The minimum weight of initiating charge of copper complex 34 for a pressed charge of RDX in a No 8 blasting cap was ~0.025-0.030 g. Minimization of the level of danger from the perchlorate complex 34 may be achieved by mixing it with an optically transparent polymer PVMT. The addition of ~10% of the polymer reduces the sensitivity to mechanical stimuli down to the level of danger for a regular organic HE, for example, PETN or hexanitrohexaazaisowurtzitane (CL-20).

The thresholds of initiation of film charges containing 90% of complex 34 and 10% of polymer PVMT by a Q-switch laser pulse were found to depend on their thickness. The thresholds increase when the thickness of the composite film charges is below 0.7-0.8 mm. Film charges having thicknesses less than ~0.15 mm were impossible to initiate by a Q-switch laser beam even with an energy density value 15 times higher than the threshold of initiation of ~1-mm samples. The experimental data allow one to suppose that the ignition of light-sensitive film composites based on complex 34 by short laser mono pulses depends on the possibility of the unloading of the material by the rarefaction waves. Complex
34 is a prospective lead-free, light-sensitive primary explosive, but the toxic perchlorate anion limits the possibility of its application in ‘green’ primers.

Conclusion

A number of lead-free, prospective primary explosives have been prepared and successfully studied in primers during recent years. However the manufacture of modern ‘green’ energetic materials on an industrial scale for practical applications in civil and military primers and detonators is still a task for the future.

Acknowledgments

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