Environmentally Friendly Energetic Materials for Initiation Devices

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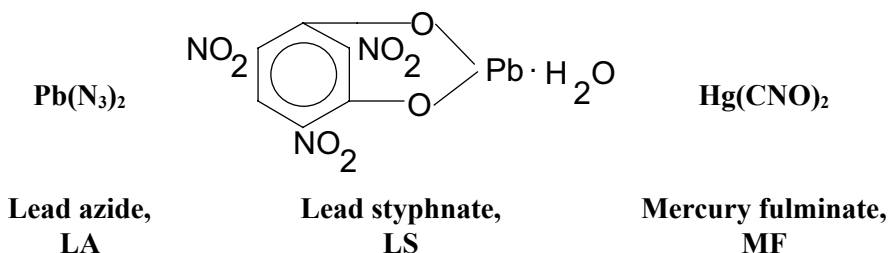
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Abstract: The problems of synthesis, properties and applications of environmentally-friendly, primary explosives are discussed. Several prospective, lead-free primary explosives have been prepared and thoroughly studied during recent decades. However, 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.

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.

$Pb(N_3)_2$ NO_2 NO_2 O $Pb \cdot H_2O$ $Hg(CNO)_2$

NO_2

Lead azide,   **Lead styphnate,**   **Mercury fulminate,**
LA   **LS**   **MF**

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, $Hg^{+2} \rightarrow Hg(R)^+ \rightarrow Hg(R)_2$ 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

Explosive	Maximum of thermal decomposition (DSC) exo., °C	Impact sensitivity, N·m	Friction sensitivity, N	Spark sensitivity, mJ	Crystal density, g/cm^2	Detonation velocity D$_p$, km/s	Initiating ability (min. charge in a No 8 detonator for Tetryl), g
LA	315	2.5 - 4	0.1	4.7	4.7	5.3	0.025
LS	282	2.5 - 5	0.1	0.2	3.1	5.2	>0.5

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

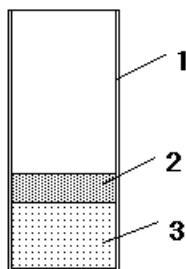pulse initiated the explosion of the primary explosive charge in the blasting cap.

Figure 1. The setup for testing the initiation ability of primary explosives.
1 – cartridge-case from No 8 blasting cap, d = 6.5 mm; 2 – charge
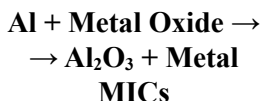of primary explosive; 3 – charge of a high explosive (HE).

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).
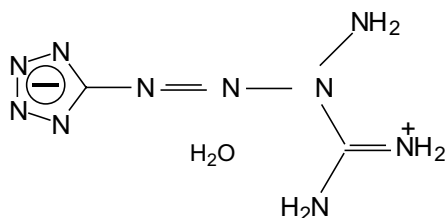
Nano-scale thermite materials

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:

$$\text{Al} + \text{Metal Oxide} \rightarrow$$
$$\rightarrow \text{Al}_2\text{O}_3 + \text{Metal}$$
$$\textbf{MICs}$$

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 [6 c]. 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.
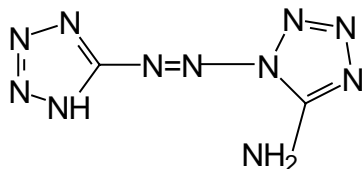
Organic compounds

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)

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 CO_2 [2]. Hence tetracene **1** does not meet requirements 1 and 3 of the LANL's criteria for 'green' energetic materials.
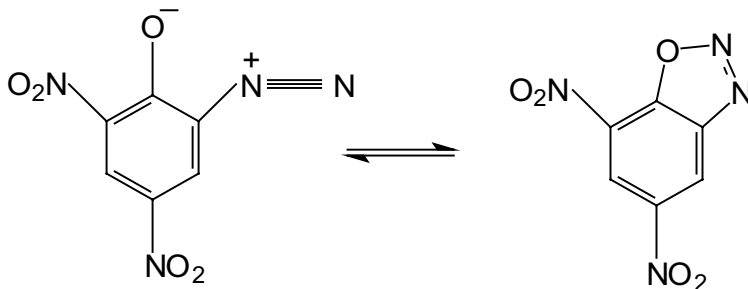
Reaction of **1** with sodium nitrite in aqueous acidic media at 70 °C affords a new energetic compound (**iso-DTET**, **2**) with a high sensitivity to mechanical stimuli. The most probable structure of compound **2** corresponds to 5-tetrazolo-azo-1'-tetrazole-5'-amine,
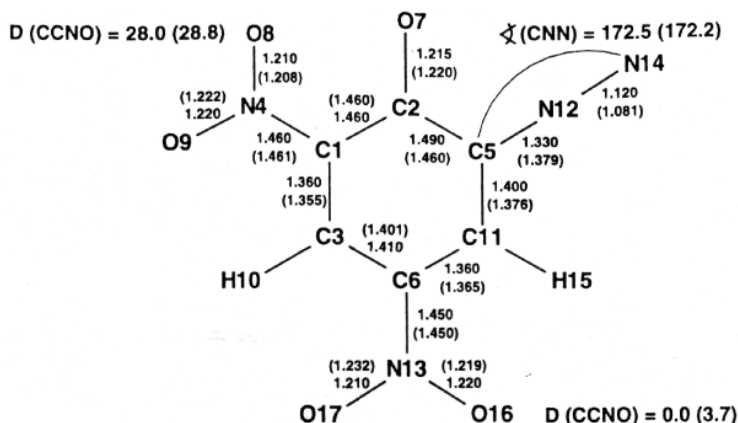
iso-DTET (2)

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-diazonio-4,6-dinitro-1-phenolate (**DDNP**, **3**) also may be considered as an environmentally friendly, energetic material.

2-Diazonio-4,6-dinitro-1-phenolate; (5,7-dinitrobenzo[d]-
[1,2,3]-oxadiazole, (3)

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 [MPWlPW91/6-31G(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.
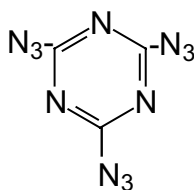
DDNP (**3**) has crystal density ~1.71g/cm³, and a detonation velocity of ~6900 m/s (at a density of 1.6 g/cm³). Its temperature of ignition is ~172 °C. The brisance of compound **3** is about 95% of that for TNT [3]. The initiation ability of compound **3** is less than that of LA. Unfortunately, this 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 ~94 °C. TAT (**4**) has crystal density ~1.73 g/cm³, detonation velocity ~ 7300 m/s (at a density of 1.5 g/cm³), and sensitivity to spark 1.2 mJ. The temperature of ignition of compound **4** is ~205 °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.
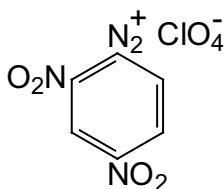

1,3,5-Triazido-2,4,6-triazine (4)

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].
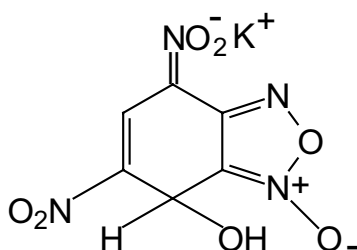

2,4-Dinitrophenyldiazonium perchlorate (5)

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.
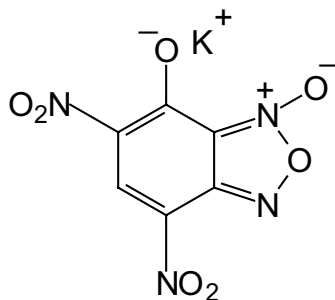
Simple inorganic salts

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)

Compound **6** has a crystal density of ~2.21 g/cm^3. 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 KNO$_3$ 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.

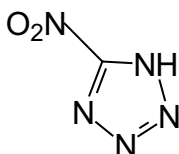Recently the potassium salt of 4,6-dinitro-7-hydroxybenzofuroxan (KDNP, **7**), a more stable salt compared to compound **6**, was prepared and studied as a 'green' replacement for LS. The synthesis of KDNP is based on KDNBF (**6**) as the starting material and it has a similar structure to compound 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^0, of 2273 kJ/kg and a detonation velocity (at density of 1.73 g/cm^3) 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.

Table 2.   Physical, chemical, and energetic properties of compounds **8-10**

Properties of the salts	**8**	**9**	**10**
Formula	CN_5O_2K	CN_5O_2Rb	CN_5O_2Cs
Mol. weight, g·mol^{-1}	153.16	199.53	246.91
Impact sensitivity, J	10	5	10
Friction sensitivity, N	<5	<5	<5
Flame sensitivity	explodes	explodes	explodes
M. p., °C	168	146	158
Onset of decomposition (DSC), °C	195	192	194
Crystal density, g·cm^{-3}	2.027	2.489	2.986

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.
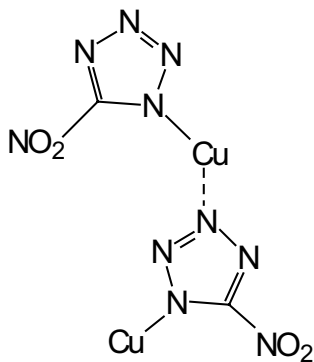
The copper (II) salt of 5-nitrotetrazole **11** is a primary explosive with high initiation ability, approximately the same as LA. Bis-(5-nitrotetrazolato)copper (II) (**Cu(NT)₂**, **11**) has a crystal density of ~2.11 g/cm^3, and the temperature of the onset of intensive decomposition is about 278 °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 ($Cu_2(NT)_2$, **DBX-1**, **12**).

Copper (I) salt of 5-nitrotetrazole, DBX-1 (12)

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].

Explosive	Maximum of thermal decomposition (DSC) exo., °C	Impact sensitivity, J	Friction sensitivity, N	Spark sensitivity, mJ	Crystal density, g/cm^3	Detonation velocity D_ρ, km/s
DBX-1, (**12**)	333	0.036	0.1	3.1	2.58	~7.0
LA	315	0.089	0.1	4.7	4.7	5.3

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].

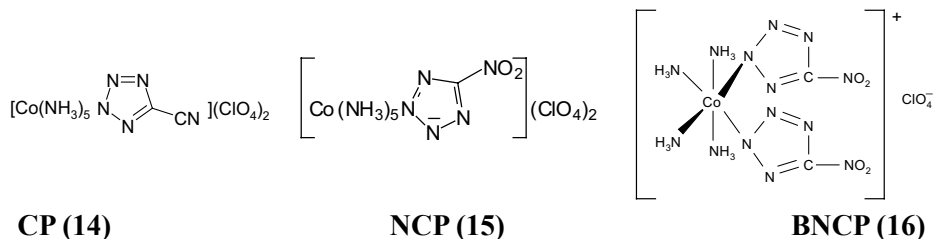**Bis(1-methyl-5-nitraminotetrazolate)copper(II) (13)**

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 $M_x(L)_y(An)_z$, where **M** is the cation of a d-metal, **L** is a ligand, **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-N²)cobalt (III) perchlorate (CP, **14**), pentaammine(5-nitrotetrazolato-N²)cobalt (III) perchlorate (NCP, **15**), and tetraammine-bis-(5-nitrotetrazolato-N²)cobalt (III) perchlorate (BNCP, **16**) are widely used in safe commercial detonators [27-29].

CP (14)   **NCP (15)**   **BNCP (16)**

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].

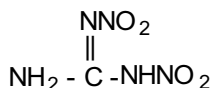**Table 4.**   Properties of complexes **15** and **16**

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

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.
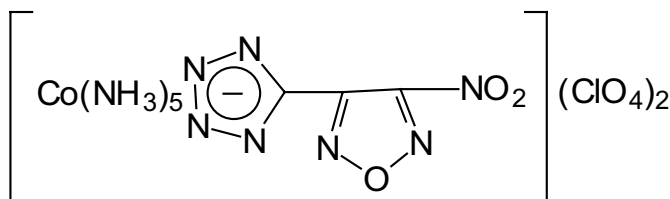
It has been found that cobalt (III) ammine coordination complex cations

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].

$$NH_2 - \overset{\overset{\displaystyle NNO_2}{\|}}{C} - NHNO_2$$

1,2-Dinitroguanidine (17)

DNG (**17**) has an enthalpy of formation of ~0 kJ/mol. The oxygen coefficient (α) 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.

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

Table 5.   Properties of complex **18**

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

The replacement of perchlorate anions by DNG anions in complex **15** was performed according to the Scheme below.

$$\left[Co(NH_3)_5 \underset{N-N}{\overset{N-N}{|\,\bigodot\,}} \text{-}NO_2 \right] (ClO_4)_2 \ + \ 2 \ NH_2\text{-}\underset{\|}{\overset{NNO_2}{C}}\text{-}NHNO_2 \ \longrightarrow$$

$$\longrightarrow \left[Co(NH_3)_5 \underset{N-N}{\overset{N-N}{|\,\bigodot\,}} \text{-}NO_2 \right] \left(\overset{NH_2}{\underset{NNO_2}{C=NNO_2}} \right)_2 \ + \ 2 \ HClO_4$$

(19)

The same method was used for the preparation of complex **20**:

$$\left[Co(NH_3)_5 \underset{N-N}{\overset{N-N}{|\,\bigodot\,}} \underset{N \ \ O \ \ N}{\diagup} \text{-}NO_2 \right] \left(\overset{NH_2}{\underset{NNO_2}{C=NNO_2}} \right)_2$$

(20)

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

$$\left[Co(NH_3)_5 \underset{N-N}{\overset{N-N}{|\,\bigodot\,}} \underset{N \ \ O \ \ N}{\diagup} \text{-}NO_2 \right] (N_3)_2$$

(21)

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

Table 6.   Properties of complexes **19-21**

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

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 °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:

$$(Cat)_{1-4}[M^{II}(NT)_{3-6}(H_2O)_{3-0}],$$

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

It was found that complexes Na$_2$[Fe^{II}(NT)$_4$(H$_2$O)$_2$] (**22**) and Na$_2$[Cu^{II}(NT)$_4$(H$_2$O)$_2$] (**23**) had the properties of primary explosives and were safer than LA or LS (Table 7).

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

Explosive	Crystal density, $\rho_{exp.}$, g/cm^3	Sensitivity to impact, cm	Sensitivity to friction, g	Sensitivity to spark, J	Onset of decomposition, °C (DSC)
22	2.2	12	20	> 0.36	250
23	2.1	12	40	> 0.36	259
LA	4.7	10	6	0.0047	315
LS	3.0	14	40	0.0002	282

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 ovepressing 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 (**Ni(N$_2$H$_4$)$_3$(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.

Table 8.   Properties of complex hydrazine nickel nitrate **24**

Complex	Crystal density, $\rho_{exp.}$, g/cm^3	Detonation velocity, $D_{(\rho)\ exp.}$, km/s	Initiation ability (minimal charge in a No 8 detonator towards PETN), g	Onset of decomposition, °C, (DTA/TG)
24	2.129	7.00 (1.7)	0.15	220

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/cm^3 (under pressure of 20-40 MPa) and ~1.70 g/cm^3 (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 $T_{ignition}$, 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 AgN_3 [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 CO_2 laser with an energy density equal to ~12.0 J/cm^2.

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(N$_2$H$_4$)$_2$](N$_3$)$_2$, 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.

Table 9.   Properties of complex bis-hydrazine nickel azide **25**

Complex	Crystal density, $\rho_{exp.}$, g/cm^3	Detonation velocity, $D_{(\rho)\ exp.}$, km/s	Initiation ability (minimal charge in a No 8 detonator towards RDX), g	Onset of decomposition, °C, (DTA/TG)
25	2.12	5.42 (1.497)	0.045	186

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 ≥ 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.
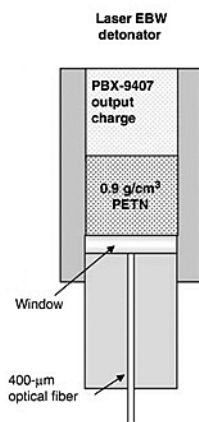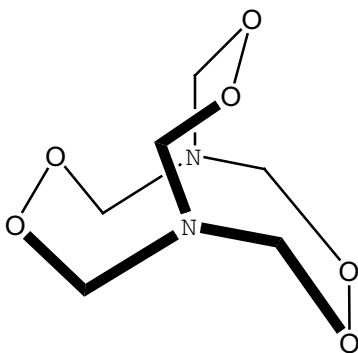

Figure 3.   Cross-section of a laser EBW detonator. The laser window is coated with a 0.25 µm layer of titanium.

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/cm³ in a laser EBW detonator is more effective than that with a bulk density of 1.0 g/cm³ [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 enviromentally 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)

Some properties of peroxide **26** are given in Table 10.

Table 10.   Properties of HMTD (**26**)

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

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

NaHCO$_3$, Na$_2$CO$_3$ and NH$_3$. Under storage, both in air and in airtight containers, hexamethylenetriperoxidediamine 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. Hexamethylenetriperoxidediamine is readily reduced with Zn metal in HCl medium, with aqueous and alcoholic solutions of SnCl$_2$ 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 hexamethylenetriperoxidediamine have a lower sensitivity to mechanical stimuli than LA and MF and can be pressed up to a density of 1.3 g/cm^3, 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/cm^2. 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 (m$_s$, mg/cm^2) 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/cm^2. 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).
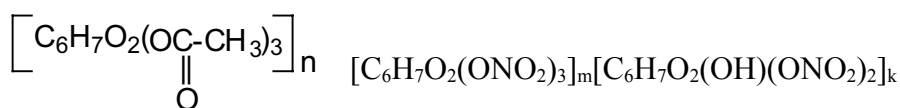
$$J = (0.0153 \pm 0.0011) \cdot m_s - (0.1203 \pm 0.0090),$$
$$n = 12, r = 0.989,$$

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.

$$\left[C_6H_7O_2(OC\text{-}CH_3)_3 \right]_n \qquad [C_6H_7O_2(ONO_2)_3]_m[C_6H_7O_2(OH)(ONO_2)_2]_k$$
$$\qquad\qquad\; \overset{\|}{O}$$

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/cm^2 results in a faster combustion than that under an energy density of 15 J/cm^2. 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 11. Some properties of copper (II) 5-chlorotetrazolate (**27**) and copper (II) 5-bromotetrazolate (**28**)

Explo-sive	Onset of decompo-sition, °C, DSC exo.	Sensitiv-ity to impact, J	Sensitiv-ity to friction, N	Sensitiv-ity to spark, mJ	Crystal density, g/cm^3	Initiation ability (min. charge in a No 8 detonator towards Tetryl), g
27	300	<1	<5	25	2.04 [51]	0.10 [51]
28	292	<1	<5	20	-	0.12 [54]

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, K_2NClO_3 (**29**) and $BaNClO_3$ (**30**) are light-sensitive, primary explosives possessing high thermal stability (Table 12) [55].

Table 12.   Some properties of salts **29** and **30** [56]

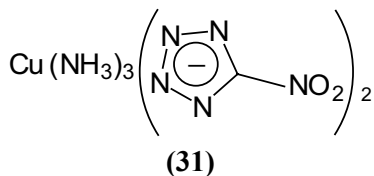| Explo-sive	Onset of de-composition exo., °C (DTA/TG)	Sensitivity to impact	Sensitivity to friction	Crystal density, g/cm^3	Initiation ability (minimal charge in a No 8 detonator towards RDX), g
29	385-390	very sensitive	very sensitive	2.70	0.10
30	350 explodes	very sensitive	very sensitive	4.62	>0.5

Salts **29** and 3**0** 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 ($\lambda = 1060$ nm, $\tau \cong 25$ 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/cm^2 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/cm^2, and for salt **30** it was ~5-7 mJ/cm^2. 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·s/cm^2) of the explosion products is related to the unit square mass (m$_s$, mg/cm^2) of the explosive (thickness of the film) through a simple equation:

$$J = (162.9 \pm 10.1)m_s - (7918 \pm 1172),$$
$$r = 0.985, \ n = 10,$$

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].
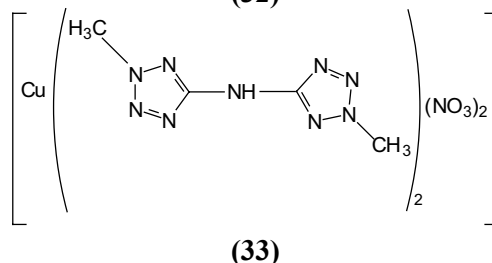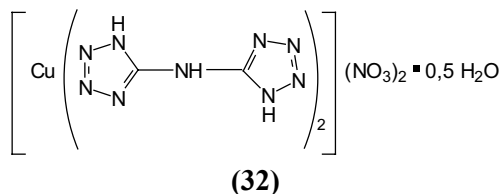
(31)

Some properties of salt **31** are shown in Table 13.

Table 13. Some properties of complex tris-amminecopper (II) 5-nitrotetra-
zolate (**31**)

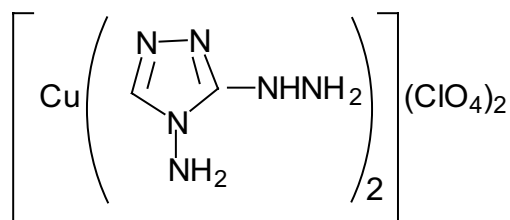| Explo-sive	Onset of de-composition exo., °C (DSC)	Sensitivity to impact, J	Sensitivity to friction, N	Sensitivity to spark (20 kV electrostatic discharge (+/-))	Thermal shock
31	245	<2	<18	-	explodes

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].

(32)

(33)

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 ($\sim 1.1 \cdot 10^{-5}$ J) by a Q-switch Nd:YAG-laser beam ($\lambda = 1064$ nm, $\tau = 30$ ns, d = 0.48 mm) [59-61].

$$\left[Cu \left(\underset{\substack{N \\ | \\ NH_2}}{\overset{N-N}{\diagup \diagdown}} -NHNH_2 \right)_2 \right] (ClO_4)_2$$

(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.

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