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Environmental Problems and Their Solutions of Using Energy-Rich Substances for Initiating Devices

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Abstract—The current state of the problem of replacing the primary explosives used in industrial products for more secure and the necessity of such a change because of the high toxicity of metals currently used in standard means of initiation are discussed. Problems of toxicity of metals used in the primary explosives are also addressed.

Keywords: Initiators, “green” explosive materials, heavy metals, mercury, lead, copper, nickel, toxicity, environmental safety.

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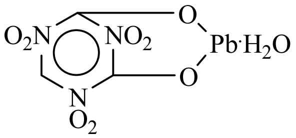
During the XX century the main initiating substances used in the mining industry, were lead azide (LA), lead styphnate (LSt), and mercury fulminate, which is now widely banned for use in the commercial means of initiation, but is produced in Russia in small quantities until now.

$Pb(N_3)_2$

Lead azide (LA)



Lead styphnate (LSt)

$Hg(CNO)_2$

Mercury fulminate

Mercury is considered to be a superecotoxicant of XXI century. According to the modern classification it belongs to the first group of extremely toxic substances [1]. Mercury is a carcinogen and the duration of its deposition in the organism may have granulomas and malignant tumors, as has been shown on animal [2]. Mercury and its derivatives are toxic to biological systems, but especially to a warm-blooded organisms, because mercury cations Hg^{+1} and Hg^{+2} readily form complexes with a variety of proteins. According to modern views, mercury and particularly organomercury compounds are enzyme poisons, resulting in inhibited action of several enzymes, that leads to the violation of main metabolic processes [3]. Under the same conditions, the degree of poisoning depends on the individual. Women and children are more sensitive to mercury poisoning [4]. Mercury compounds also are toxic for the nervous system. In chronic mercury poisoning occurs in humans appearance irritability sequences, and the dream is broken, weakened memory [5]. Chronic action of mercury salts on warm-blooded organisms causes multi-functional disorders of the nervous system, reduced visual acuity and trembling limbs [6]. In the marine ecological systems, mercury cations are easily converted into alkylated forms of $Hg^{+2} > Hg(R)^{+} > Hg(R)_2$, which are much more toxic than the original mercury cations [7]. These organomercury compounds remain in the body significantly longer than the simple salts and their excretion is extremely challenging. As a result of chronic mercury poisoning violations occur in the cardiovascular system: slowed or accelerated heart rate, decreased blood pressure, due to the blockade of SH groups of vessel wall chemoceptors [8]. Mercury and its compounds affect the sex glands and fetus, causing birth defects. Mercury poisoning is accompanied by hearing loss, speech disorder, pains in the limbs [9]. These phenomena are practically irreversible and require long-term treatment, at least to reduce them. These symptoms may appear after months or even years after exposure [8]. Particularly pronounced are manifestations of methyl mercury poisoning [10], which high toxicity even in small doses caused by the ability to pass through biological membranes, to get into the brain and spinal cord, pass through the placental barrier [11]. Mothers who underwent light mercury poisoning, gave birth to children with cerebral paralysis. In nursing mothers mercury gets into breast milk and then into the blood of infants [12].

In the problem of mercury poisoning a special place is occupied the question of micromercurisation – a complex of pathological changes that arise as a result of prolonged exposure of an organism to mercury vapor at very low concentrations [13]. There are several degrees of micromercurisation. The first degree is characterized by a decrease in performance, fatigue, increased excitability. At the second level, these phenomena become more pronounced, appear headaches and unwarranted anxiety. Under chronic mercury poisoning it accumulates in the body [4].

Using of hundreds of millions of blasting caps (BC), electric detonators (ED) and the primers containing LA and LSt has led to hundreds of kilograms of lead superecotoxicants fall annually into the environment, causing damage to both ecosystems and the staff. Thus, a 1991 year survey of the FBI shooting range in Quantico, Virginia, United States, revealed an excess of lead level in the blood of civil servants by 10 times in comparison with the federal health standard [14]. Lead, along with cadmium and mercury form the “dismal three” most toxic non-ferrous industrial metals [15]. Lead is a particular threat to women, because it has the ability to pass through placenta [16] and also accumulates in breast milk [17]. It is shown that in chronic lead intoxication in women immunity drops dramatically [18] and significantly increases the number of gynecological diseases. Lead actively affects the protein biosynthesis, energy metabolism and genetic apparatus in the cell [19], inhibits several enzymes involved in the porphyrins biosynthesis, thereby blocking it. Lead also inhibits the activity of SH-containing enzymes causing significant deviations in the lipid metabolism, increasing the plasma levels of total, non- protein, cholesterol [20]. It is believed that lead predisposes to the development of atherosclerosis. Children are more sensitive to the toxic effects of lead than adults [21, 22]. Lead actively accumulates in bone tissue [23, 24]. Besides bones, lead deposits in the spleen, liver, kidney, brain and other organs [23]. It affects the cardiovascular system causing the heart diseases [25] High lead concentrations, inhibiting the processes of tissue respiration, phosphorylation and active transport, cause functional and morphological changes in the mitochondria. Lead toxicosis actively affects blood forming organs [26], the nervous system and kidneys [27]. Life expectancy of red blood cells drops, potassium ion passage from red blood cells into the plasma is increasing, which ultimately leads to lysis of red blood cells. A direct correlation was found between the level of lead in drinking water and the development of arterial hypertension [28]. Lead also has a negative impact on the sexual sphere [29]. The consequence of the toxic effect of lead on male reproductive function are functional deviant behavior disorders up to infertility, as well as changing the hereditary status, manifesting in children health problems[30]. Among the syndromes of lead poisoning one of the leading places occupied by the changes in the gastrointestinal tract [31]. Due to the inhibitory effect of lead on the intestinal enzymes, parietal digestion processes is broken[32]. Sometimes lead intoxication leads to intestinal colics, reduced gastric secretion, violation of motor-evacuation function of the intestine [27].

Under chronic lead poisoning chronic hepatitis develops. Lead is able to activate the generation of reactive oxygen forms, thus stimulating peroxidation damage to key biopolymers [33]. Experiments have shown that lead can initiate apopthosis. One of the induction mechanism is the lead activation of Ca,Mg-dependent endonuclease. Lead inhibits the oxidation of fatty acids, disrupts lipid, carbohydrate and protein metabolism, causes a change in the electrical and mechanical activity of the heart muscle, vascular damage and impaired vascular tone [34]. Particular toxic to the nervous system are organic lead compounds, as they suppress the metabolism of glucose, synthesis of RNA and DNA, damage myelin sheaths of nerve cells that accompanied by a change in the rate of transmission of nerve excitation. For example, tetraethyl lead significantly alters the metabolism of serotonin and noradrenaline, increases pyruvate level in blood, leading to disruption of oxygen supply to the brain [35]. From the human body lead is excrected mainly in the urine (75–80%) and the feces (15%). On the basis of the foregoing, the lead should be attributed to superecotoxicants. Having summarized the facts, lead compounds affect these vital systems:

(1) Haematopoietic system. Under chronic lead poisoning develops anemia, decreases the number of red blood cells and hemoglobin level in the blood.

(2) Lead and its compounds act on the central nervous system, causing violations of long-term

memory [36]. Especially sensitive to such effects are children and adolescents. Children living in areas polluted with lead have sharply reduced ability to learn [37].

(3) Lead actively accumulates in bones, replacing calcium, which leads to osteoporosis, accumulates in the teeth tissues [24]. The elimination half-time from bones is more than 25 years.

(4) Lead belongs to thiol poisons, actively binding with SH-groups of many proteins, which lead to the disruption of the metabolic processes .

Especially dangerous lead contamination of terrestrial ecosystems, as it is actively concentrated and retained in the soil, being transferred to plants and thus actively involving in the food chain.

Systematic studies on the synthesis of low-toxic, environmentally friendly ("green") initiating-controlling substances intended to replace the LA and THPC in the initiators were held after the signing in 1993 by President Bill Clinton of special laws that reduce or even preclude procurement of hazardous substances and materials for the needs of the federal government. At the end of the XX century, a number of countries have adopted national programs to reduce and/or eliminate the use of lead salts in civil detonators. In 2006, researchers at the Los Alamos National Laboratory (LANL, USA) have been published very strict requirements for environmentally friendly energy-rich substances, intended to replace the lead azide and styphnate in civilian BC, ED and HFs [14]. The ideal "green" initiating substance, from the point of view of LANL scientists should meet the following six criteria:

(1) be insensitive to moisture and light;

(2) do not have too high sensitivity to mechanical impact and static electricity so that substance can be processed of transported;

(3) have a thermal stability at least up to 200°C;

(4) initiating material should be chemically stable during long-term storage;

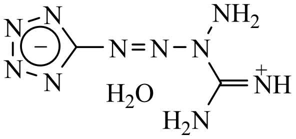
(5) "green" initiating materials should not contain toxic metals of the first toxic group;

(6) energy-rich initiating substance should not contain perchlorate, which is probably a teratogen (causes malformations during fetal development) and has a detrimental effect on the thyroid gland.

Existing initiating energy-rich substances include: organic substances, simple inorganic salts, metal complexes and nanothermite mixtures.

Thus, the metastable mixture of aluminum nanopowders and heavy metal oxides are thermostable, have the required level of sensitivity and can in principle be used as the means of initiation. Unfortunately, their instability when stored on air and in the presence of moisture, security problems in industrial production, as well as the presence of highly toxic heavy metals in the solid residues of explosion products points to the futility of this trend in production of a "green" triggering substances.

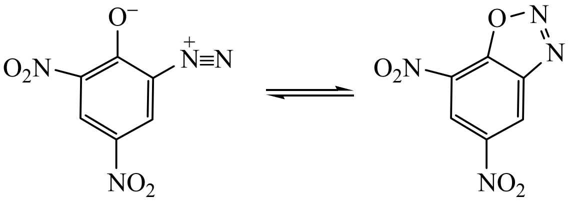
Of the standard used triggering substances only tetrazene [1-(5-tetrazolyl)-3-guanyltetrazene hydrate] (**I**) can be attributed to the environmentally friendly compounds, because it contains no toxic metal ions and perchlorate [38–40].



I

Flash point of tetrazene at 5 s discharge delay is ~160°C, the temperature of starting intensive decomposition ~140°C. When heated above 60°C, it slowly degrades, and is destroyed by carbon dioxide in the presence of moisture. Tetrazene decomposes in boiling water [40]. Therefore, the compound **I** do not meet modern requirements for "green" TRS in terms of chemical resistance and thermal stability.

Other organic compounds with a short section of deflagration to detonation transition also mostly do not meet modern requirements for thermal stability. For example, 2-diazo-4,6-dinitrophenol (**II**) has been used in China as the main triggering agent for industrial BC and ED, and in Europe as a component of non-toxic primers for small arms [41]. Both open and cyclic structure for **II** is proposed.

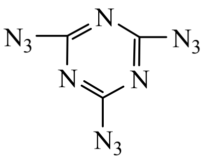


II

According to the results of X-ray diffraction and quantum chemical calculations (method [MPWlPW91/6-31G(d,p)]), most likely this compound exists as an open structure [42].

Unfortunately, this compound darkens rapidly under sunlight and also causes the development of allergic symptoms. Therefore, the compound (**II**) does not meet modern requirements for "green" triggering substances.

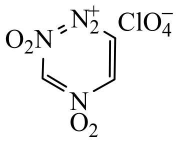
Low toxic substance is effective initiating cyanuric triazide (2,4,6-tri-azido-1,3,5-triazine, **III**) [38, 43, 44].



III

However, it is noticeable volatile at temperatures above 30°C, decomposed by hot water, and above a temperature of 100°C loses stability even in dry state. Cyanuric triazide **III** did not find practical application due to high volatility. Compound **III** also does not meet modern requirements for "green" triggering substances and can not be regarded as a promising enviromently friendly initiating explosive.

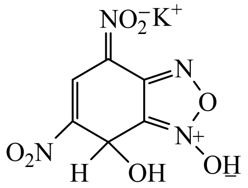
2,4-dinitro-phenyldiazonium perchlorate **IV** has been proposed in Russia as an effective low-toxic substance for industrial initiating BC and ED [45, 46].



IV

Flash point of salt **IV** is ~218°C. However, perchlorate **IV** is hygroscopic and loses the ability to initiate at high humidity. In addition, it contains toxic perchlorate anion. Therefore, this compound does not meet the 6th requirement of American researchers to the "green" initiating substances.

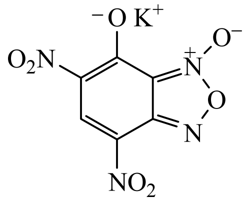
Potassium 4,6-dinitro-7-hydroxy-7-hydrobenzofuroxan (KDNBF, **V**) is a low-toxic "pseudoinitiating" substance [47–49].



V

Flash point of KDNBF at 5 s delay is 207–210°C, the temperature of staring intensive decomposition ~190°C. KDNBF is used in the United States in the low-toxic ignition pyrotechnic compositions with non-toxic oxidant KNO3 and additives that increase the susceptibility of structures to shock and friction. Pilot production of KDNBF was launched in the U.S. shortly after the Second World War. Product **V** can be considered as a viable candidate in the "green" energy rich material for HF and BC. However, a significant disadvantage of **V** is its insufficient heat resistance.

Recently, potassium salt of 4,6-dinitro-7-hydroxy-furoxan (KDNP, **VI**) has been obtained and investigated as a possible "green" substitute for LSt.

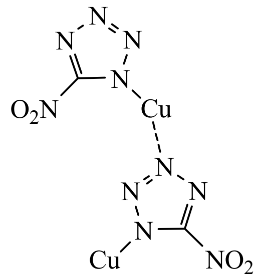


VI

Unlike KDNBF **V**, which is a Meisingeimer complex, KDNP is a simple salt. The temperature of starting intensive decomposition of salt **VI** is about 270°C [50] . The substance is fastburning with good thermal stability and fairly safe to use. Since 2009 KDNP **VI** is approved for use in the U.S. Army Ordnance ammunition .

Search for low-toxic initiating substances forced researchers to return to the salts of 5-nitro tetrazole (HNT) as one of the most energy-rich anions forming a stable ionic compounds [44]. Bis(5-nitrotetrazolate) copper(II) [$Cu(NT)_2$, **VII**] as the triggering substance comparable to lead azide. Salt has T_{nir} = 278°C. Bis(5-nitrotetrazole) copper **VII** is recommended as a promising low-toxic substances for fuzes. An experimental technology is developing in the United States to produce the salt **VII** [51, 52], which will replace the highly toxic primary explosives in a number of products.

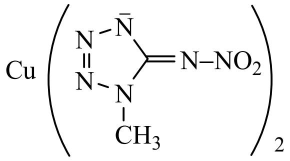
Another initiating material which can replace LA in low emission detonators is copper(I) salt of 5-nitrotetrazole [$Cu_2(NT)_2$, DBX-1, **VIII**].



VIII

Temperature of beginning of intensive decomposition of **VIII** is about 333°C (DSC). An experimental industrial technology for production **VIII** is also currently being developed in the United States [53].

Another low-toxic agent for the means of initiation is copper bis(1-methyl-5-nitroaminotetrazole) (**IX**) [54].



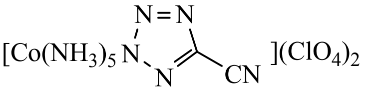
IX

Temperature of beginning of intensive decomposition of copper salt **IX** is ~252°C. The material withstands thermostating at 190°C for 48 h without changes in the properties, which means it is sufficiently thermostable. On the real prospects of using **IX** in commercial products only could be judged after an extended series of tests. However, the presence of copper in the proposed compounds also have a negative impact on living organisms.

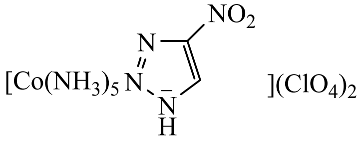
Despite the fact that copper belongs to the so-called biometals, in high concentrations it is quite toxic to most of the organisms and environmental systems [15]. High concentrations of copper stimulate the generation of reactive oxygen forms that leads to oxidative damage of proteins and nucleic acids. However, copper deficiency leads to inactivation of key antioxidant enzymes and leads to disruption of the energy processes in living systems [11]. Significant copper deficiency in humans and animals can cause anemia, decrease in the intensity of growth, loss of body weight and the acute shortage of metal (less than 2–3 mg per day) may cause rheumatic arthritis and endemic goiter. Excessive uptake results in copper human Wilson's disease in which the excess element is deposited in the brain tissue, skin, liver, pancreas and myocardium [15]. Thus, optimal concentration of copper should be maintained in ecosystems, since it is required for the normal functioning of all organisms in the biosphere.

Replacement of lead and mercury for copper in primary explosives became trendy in the development of safer explosives and can be considered as the first step to so-called "green" primary explosives.

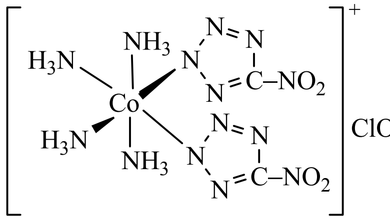
It is well known that such a complex perchlorates of cobalt(III) amminates as pentaammin (5-cyanotetrazole-N^2) cobalt(III) perchlorate (CP, **X**), pentaammin (5-nitrotetrazolato-N^2) cobalt(III) perchlorate (NCP, **XI**) and tetraammin bis(5-nitrotetraze-N^2)cobalt(III) perchlorate (BNCP, **XII**) found practical use in "safe" BCs and EDs [55–57].



X



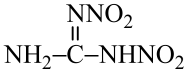
XI



XII

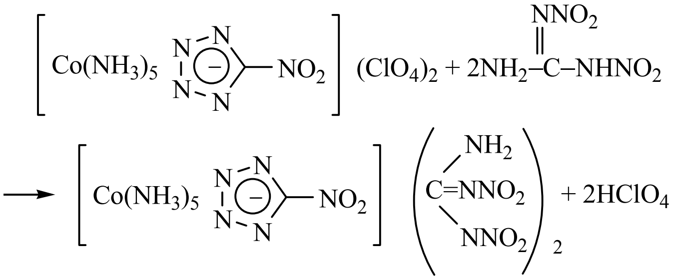
Complex perchlorates of cobalt(III) amminates with tetrazole ligands are heat resistant, non-hygroscopic and safe enough. These substances do not contain highly toxic heavy metals. But these cobalt complexes do contain biologically dangerous perchlorate anion. Also: dermatitis, asthma, respiratory hypersensitivity, diffuse nodular fibrosis are potential diseases caused by high content of metallic cobalt in the environment resulting from the use of these complexes. Therefore, complex perchlorates of cobalt(III) amminates with azole ligands also can not be referred to as "green" triggering substances [14].

Replacement of the perchlorate anion in cobalt(III) amminates for another, more environmentally friendly oxidant anion can reduce the toxicity of metalcomplexes, saving a short section of the deflagration to detonation transition. This assumption has been experimentally verified by the synthesis and study of the properties of cobalt(III) complexes with dinitroguanidine (DNG) [58].



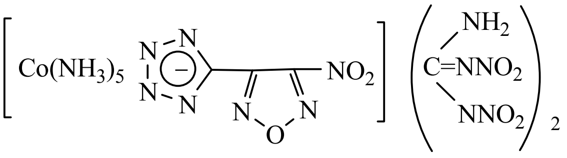
$$NH_2\text{–}\overset{NNO_2}{\overset{\|}{C}}\text{–}NHNO_2$$

DNG is a good complexing agent, has zero enthalpy of formation, is an oxidant (oxygen ratio DNG : α = 1.14; oxygen ratio of DNG-anion : α = 1.33) [59, 60]. As initial complex perchlorates cobalt pentaamminates with T_{decomp} 265–280°C were selected. Dinitroguanide cobalt(III) complex **XIII** was isolated according to the following scheme:



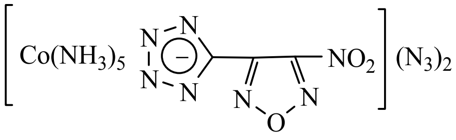
XIII

Similarly, has been prepared complex **XIV** with tetrazole-5-(4-nitrofurazan-3-yl) in the inner sphere.



XIV

Complex **XV** with sodium azide was synthesized with 5-(4-nitrofurazan-3-yl) tetrazole in the inner sphere:



XV

Studies showed that the DNG anion was less effective oxidant of the inner sphere of the complex amminate **XIII**, than the perchlorate anion in the NCP complex, **XI**. Replacement of the perchlorate anion for the anions of DNG and N_3 leads to an increase of deflagration to detonation transition section in complexes **XIII–XV** and reduces the effectiveness of the complexes as primary explosives.

Investigation of the thermal decomposition of these complexes by DTA at a sample heating rate of 5 K/min showed that substitution of the perchlorate anion for DNG or azide anion reduces Tnir for 80–100°C, due to decomposition of the outer-sphere anion, which is catalyzed by a cobalt(III) ion and ammonia emitted in the first stage of decomposition [61]. Consequently, the complexes **XIII–XV** do not satisfy the requirements for “green” explosives neither for thermal stability, nor in efficiency.

Meanwhile, search for “green” energy-rich substances continues, including complex salts of 5-nitrotetrazole. Researchers at Los Alamos National Laboratory proposed copper and iron complex salts of HNT [14] as the ideal “green” initiating agents to meet all 6 their criteria.

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

Cat = NH_4, Na, M = Fe, Cu.

The authors argue that the performance properties of these metal complexes are asily regulated by proper chose of the Cat and M, and the content of the NT in the molecule. Tests have shown that the experimental BC and ED containing initiate charges of complexes

$Na_2[Fe^{II}(NT)_4(H_2O)_2]$ (**XVI**)

or $Na_2[Cu^{II}(NT)_4(H_2O)_2]$ (**XVII**)

in characteristics do not differ from regular ones, filled with lead azide, but industrial production of these complexes probably doesn't exist so far. Another group of complexes under consideration as potential replacements for mercury and lead-containing primary explosives are nickel complexes.

The fact that nickel hydrazinates with anions-oxidants have a short section of the deflagration to detonation transition, and can be used to initiate energy-rich organic substances is known for a hundred years already [44]. However, these compounds are less effective than lead azide, so until recently, the possibility of their practical application in the BC and ED had not been considered. Search for environmentally-friendly energy-rich compounds that are not harmful to the environment, has forced researchers to return to this class of metal salts. One of the promising "green" energy-rich compounds that can replace lead azide in commercial BC and ED, is an complex nickel(II) hydrazine nitrate **XVIII** [62, 63], that can be prepared from readily available raw materials in the standard equipment in an aqueous medium at a temperature of 65°C by the following reaction:

$$\mathrm{Ni(NO_3)_2{\cdot}6H_2O + 3N_2H_4{\cdot}H_2O \rightarrow \underset{\textbf{XVIII}}{Ni(N_2H_4)_3(NO_3)_2} + 9H_2O.}$$

Complex **XVIII** is not hydroscopic and practically insoluble in water, resistant to sunlight and X-rays, not very sensitive to the charges of static electricity. Flash point for nickel complex **XVIII** at 5 s delay is ~167°C. Temperatures of the beginning of the decomposition and the temperature began intensive decomposition determined by DTA, are 210 and 220°C, respectively. China has developed a technology for industrial producing of complex **XVIII** to securely receive up to 20 kg of the product in a single deposition. The complex **XVIII** is used in China in environmentally friendly industrial BCs and EDs.

Complex azide of hydrazonickel(II) **XIX** - another candidate for the replacement of lead azide in the "green" industrial BCs and EDs [64]. Product **XIX** is prepared from nickel acetate or nitrate, hydrazine and sodium azide, by the following reactions:

$$\mathrm{Ni(NO_3)_2{\cdot}6H_2O + 2N_2H_4{\cdot}H_2O + 2NaN_3}$$
$$\mathrm{\rightarrow \underset{\textbf{XIX}}{[Ni(N_2H_4)_2](N_3)_2} + 8H_2O + 2NaNO_3}$$

or

$$\mathrm{Ni(CH_3COO)_2{\cdot}4H_2O + 2N_2H_4{\cdot}H_2O + 2NaN_3}$$
$$\mathrm{\rightarrow \underset{\textbf{XIX}}{[Ni(N_2H_4)_2](N_3)_2} + 6H_2O + 2CH_3COONa}$$

Nickel complex **XIX** is a green polycrystalline product. Technical product is not hygroscopic and insoluble in water. Flash point at 5 s delay is ~193°C. An experimental technique of obtaining complex **XIX** is developed in China, to securely receive up to 5 kg a batch of product. Tests of ED, containing complex **XIX** as PCR, showed that they are not inferior to the regular ED and may be used in the mining industry.

Thus, in the XXI century China developed Industrial technology of the two "green" energy-rich metal complexes for initiating: $\mathrm{Ni(N_2H_4)_3(NO_3)_2}$ **XVIII** and $\mathrm{[Ni(N_2H_4)_2](N_3)_2}$ **XIX**. Unfortunately, the thermal stability and the initiating ability of the complexes **XVIII** and **XIX** do not meet modern requirements for "green" energy-rich initiating substances.

Furthermore, nickel is an active carcinogenic agent. The toxicity of nickel to plants is manifested in the suppression of photosynthesis and transpiration, the signs of chlorosis of leaves. For the animals, toxicity is accompanied by a decrease in activity of a number of metalloenzymes, disturbance of protein, RNA and DNA synthesis, damage expressed in many organs and tissues [15]. Experimentally established embriotoxitity of nickel. Excessive intake of metal in animals and humans may be associated with an intense anthropogenic pollution of soils and plants [13].

The relatively low mobility of the metal causes its fairly uniform distribution in natural environments. Therefore, with high content of nickel in the environment due to massive use of complexes **XVIII** and **XIX** in the BCs and EDs the adverse effects on living organisms will last for a long time.

In conclusion, it should be noted that the search for "green" energy-rich compounds is performed in various countries. There have been appeared ways to approach the solution of this problem, there are some achievements. But the optimal solution to the problem of creating non-polluting initiationg substances, confirmed by commercial release of industrial "green" fuses and primers is not available yet.

ACKNOWLEDGMENTS

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