Thermoplastic Explosive Compositions on the Base of Hexanitrohexaazaisowurtzitane

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Abstract. Hexanitrohexaazaisowurtzitane is an azostructural compound known as CL-20. We performed a series of experiments with CL-20 synthesized in Russia to evaluate the possibility to use it in pressed high explosive compositions. We used it in thermoplastic compositions both with an inert binder and energetic binder. The compositions were conventionally named CL-20И and CL-20A. It was determined that the thermoplastic compositions had the most high detonation parameters and a level of sensitivity to mechanical effects acceptable to allow their processing. Their detonation characteristics were compared with that of some known foreign compositions based on CL-20.

Keywords: explosives, CL-20, hexanitrohexaazaisowurtzitane, thermoplastic compositions, explosive characteristics.

Among investigations of synthesis of explosives, which meet different operational requirements, particular interest is paid to the works concerning new high explosives with significantly higher energetic characteristics than that of HMX, capabilities of which practically completely realized both in high explosive and in solid propellant compositions.

From the achievements of last decades it is worth to pay attention to Nilsen synthesis of skeleton azo compound – hexanitrohexaazaisowurtzitane (HNIW), well known as CL-20, in 1987 in the USA. CL-20 molecular structure is a space isowurtzitane lattice in which to each bridge atom of nitrogen one nitro group is attached. Without going into details we note that HNIW synthesis is a labour-consuming process usually consisting of glyoxal condensation with benzyl amine followed by debenzylation through catalytic hydration in the presence of acetic anhydride followed by nitration in two steps. The most successful in practical realization of CL-20 production process were Thiokol Corporation (USA), SNPE (France) and Bofors Explosives AB (Sweden).

Owing to flexible conformational structure CL-20 molecules are capable to form a number of rather stable polymorphs. On the base of investigations of CL-20 six nitro groups orientation symmetry relative to stable isowurtzitane skeleton and existing steric difficulties foreign researchers assume that there exist 12 conformation forms. From derived pure polymorphs there were reliably identified four polymorphs of CL-20 (Table 1) among which ε-form with mono crystal theoretical maximum density of 2.044 g/cc was of practical interest. According to the available results of foreign investigations real density of CL-20 ε-polymorph particles measured by flotation

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TABLE 1. CL-20 Polymorphs Properties.

Polymorphs	Space groups	ρ, g/cc	ΔH$_f$, kcal/mol	Increase of thermo-dynamic stability
β	Pb2$_1$a	1.99	-	↓
α (hydrate)	Pbca	1.97	82	
γ	P2$_1$/n	1.92	-	
ε	P2$_1$/n	2.044	95	

method is within the range of 2.033-2.038 g/cc. It is considered that this CL-20 polymorph (monoclinic space group P2$_1$/n) is the most stable thermodynamically in normal conditions.

CL-20 tendency to have polymorphs is its significant disadvantage. Non-reversible transformations of ε-polymorph to γ-polymorph were registered both at high (136-140^{o}C, 152-183^{o}C) and at rather low temperatures (55-58^{o}C, 63-65^{o}C) depending on crystals sizes, their defects, presence or absence of a solvent, rate of heating and time of standing. Such transformations, a polymorph kind and particle size depend also on conditions of CL-20 crystallization from saturated solutions: temperature, nature and purity of used solvents and precipitants. It is worth to note that CL-20 α-polymorph exists only as crystalline hydrate and a number of researchers found some amount of hardly removable water even in ε-polymorph.

CL-20 is rather thermostable: active solid phase self-increasing decomposition of its γ-polymorph is observed within the temperature range of 225-235^{o}C and it is nearly 30-35^{o}C lower than that of HMX. At low pressures CL-20 flameless combustion is observed with nearly 700^{o}C temperature and formation of structural solid residue.

Characteristic properties of this explosive are high detonation velocity and pressure in combination with high crystal density and favorable enthalpy of formation (Table 2).

TABLE 2. Comparative calculated properties of PETN, RDX, HMX and CL-20.

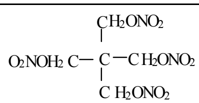
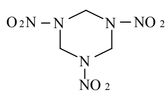
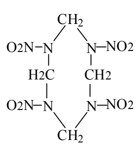
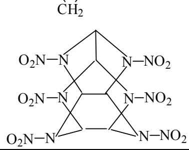
Name	Formula	α	ρ, g/cc	ΔH$_f$, kcal/mol	D, m/s	Q, kcal/kg	Pdet, kbar
PETN		0.860	1.778	-126	8200	1390	290
RDX		0.667	1.820	16	8760	1320	326
HMX		0.667	1.904	20	9000	1340	364
CL-20		0.800	2.044	95	9530	1430	444

TABLE 3. Granulation of tested CL-20 sample.

Particles retained on a screen, %				**Passing screen particles, %**
250 μ	160 μ	100 μ	50 μ	50 μ
0.4	1.8	36.2	53.0	8.6

TABLE 4. Experimental Parameters Of Tested Explosives.

Name	**Real density of crystals, g/cc**	**Lower level of impact sensitivity,mm**	**Rate of explosions,%**	**Lower level of friction sensitivity,MPa**	**Critical thickness of detonation wave, mm**
PETN	1.77	50	100	150	0.22
RDX	1.80	70	72	270	0.48
HMX	1.89	50-70	80	200-250	0.55
CL-20	2.04	<50	80	100	0.20

We carried out a number of experiments to determine the possibility to use CL-20 in high explosive compositions applicable for pressing. In the experiments CL-20 synthesized in Russian Federation was used with the following particle size (Table 3).

At first CL-20 X-ray crystal structure was determined that showed its correspondence with ε-polymorph and then CL-20 sensitivity to external mechanical effects.

The results in Table 4 show, that real crystal density of this CL-20 sample corresponds to that of its ε-polymorph too. Levels of sensitivity to external mechanical effects and of detonation wave critical thickness are close to that of PETN and acceptable to process CL-20 with observing safety rules. At the same time CL-20 is a stable explosive and compatible with usual components of compound solid propellants and explosive compositions.

On the base of CL-20 thermoplastic compositions were prepared both with an inert binder (acrylic polymer and wax) and an energetic binder (TNT and mixed vinyl polymer). The compositions were named CL-20И and CL-20A. CL-20И was prepared using water-emulsion process and CL-20A by water-suspension process with an organic solvent. The results of tests for critical thickness of detonation wave, sensitivity to mechanical effects of the compositions, their pressing ability at different temperatures, detonation velocity of charges with 10mm diameters are shown in Table 5.

It is seen that the model thermoplastic compositions have at present the highest detonation parameters and sensitivity to mechanical effects acceptable for processing. And it is worth to note that detonation velocities of CL-20И and CL-20A are evidently not ultimate because they were determined with the charges of small diameters. In this connection the calculations were made of these compositions detonation velocities in the charges with obtained densities taking into account real maximum values and calculations of amour penetration (L) and acceleration impulse (η) relating to the most powerful foreign thermoplastic composition LX-14 on the base of HMX (Table 6).

TABLE 5. Experimental values of CL-20 model thermoplastic compositions characteristics.

Composition name	**Content of components %**	**Lower level of impact sensitivity, mm**	**Lower level of friction sensitivity, MPa**	**Density of charges at $P_{sp.}$=200MPa and pressing temperature g/cc**	**Critical thickness of detonation wave, mm**	**Detonation velocity of Ø10mm charges (at density, g/cc), m/s**
CL-20И	CL-20 – 98 Inert binder – 2	70	200	20°C–1.875 (6.5) 95°C-1.966 (1.9)	0.20	9170 (1.966)
CL-20A	CL-20 – 98 Energetic binder – 2	50	150	20°C-1.850 (8.7) 95°C-1.999 (1.3)	0.19	9230 (1.999)

TABLE 6. Comparative properties of high explosive thermoplastic compositions.

Name	**Components %**	**ρ, g/cc**	**D, m/s**	**Q, kcal/kg**	**$P_{sp.}$, kbar**	**Amor penetration L, %**	**η, %**	
							Radial propelling	**End propelling**
LX-14	HMX – 95.5 Estane – 4.5	1.835	8790	1210	315	100	100	100
CL-20И	CL-20 – 98 Inert binder – 2	1.966	9190	1380	380	111	107	108
CL-20A	CL-20 – 98 Energetic binder – 2	1.999	9350	1390	400	115	109	110
LX-19	CL-20 – 95.8 Estane – 4.2	1.929	9130	1350	360	108	105	106
PATHX-2	CL-20 – 95 Estane – 5	1.923	9120	1330	355	108	104	105
PBXC-19	CL-20 – 95 Ethyleneviny l acetate – 5	1.896	9080	1330	345	106	103	104

The results of Table 6 confirm the advantages of the model compositions CL-20И and CL-20A, as well as some foreign compositions based on CL-20, according to their detonation properties in comparison with LX-14. Substitution of HMX with CL-20 (kind and quantity of a binder, conditions of making charges leaving without change) increases detonation velocities of the charges by 300-350m/s and explosion heat by 100-150kkal. In every case of substitution it is necessary to take into account a sufficiency of CL-20 energetic advantages as well as available information about its operational characteristics when formulating high-energy compositions.