STUDY INTO THE INFLUENCE OF TEMPERATURE AND TIME FACTORS (160°C, 1-7 DAYS) ON HMX STRUCTURE
(#254)

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This paper presents the results of studies into temperature and time effects (160°C, 1-7 days) produced on HMX. HMX crystals ($C_4H_8O_8N_8$) of β form having $S_{sp} \sim 300 cm^2/g$ and $S_{sp} \sim 300 cm^2/g$ specific surface area were chosen as the subject of investigation to study HMX phase transition conditions. To study HMX structure and its physical and chemical properties, such techniques as optical microscopy, thermography, IR spectroscopy, X-ray analysis and a pycnometric density determination method were used. It has been shown that HMX experiences no polymorphic transformation at 160°C close to the shooting apparatus operation temperature and after 1-7 days of its aging. It has been found out that heating at 160°C during 7 days results in decrease in the density of HMX crystals from $1.901 g.cm^3$ to $1.801 g/cm^3$. Even on the first days of thermal aging large HMX crystals ($S_{sp} \sim 300 cm^2/g$) have many internal and surface defects and become turbid. All these effects are the result of complicated processes proceeding in the crystal "body" during thermal aging. The change in the microstructure and density of the studied HMX crystals made it possible to assume that there are "retained" gases in the crystal "body". It has been shown that "retained' gases may be produced in HMX crystals.

INTRODUCTION

It is known that HMX is unrivalled among other explosives in its practically important characteristics such as power, density, thermal stability, etc[1,2]. Specialists of VNIIEF and VNIITF contributed greatly into studies of HMX-based explosive compositions in the 60s-80s and they continue solving various technological and other problems now facing

the domestic industry. In particular, the spread of conversion activities aimed at developing thermally stable compositions for shooting apparatus (SA) and EC operation systems used in petroleum and gas extracting industries has been expanded[3]. For the HE containing SA used in the oil and gas industry the problem of study into its ultimate operation abilities at elevated temperatures has become urgent in recent years. This is explained by a few reasons, the main of which are as follows:

-oil and gas are extracted from increasingly deep strata whose temperature is as high as $\sim 200°C$ and over;

-HMX being the filler of many explosive compositions used in SA experiences polymorphic transformations at $180°C$ which change greatly physical and chemical properties of HE.

Until now the information about phase transformations in the HMX samples under study and its upper operation limit had a rather contradictory character although much has been done in this area. This points to the fact that specific problems of HMX application under the given high temperature and time effects should be solved through combined studies using up-to-date physical and chemical methods such as optical and electron microscopy, temperature recording, IR-spectroscopy, X-ray analysis and a pycnometric density determination method. Thus, study of HMX phase transitions is a topical problem because clear, scientifically substantiated knowledge of the limits of HMX probable application in its various forms is required.

Additional checking of temperature and time effects produced on the possibility of HMX polymorphic transition was the aim of this work. The initial temperature of $160°C$ and the aging time of 1-7 days were chosen for studies.

HMX crystals of β form having $S_{sp} \sim 300cm^2/g$ and $S_{sp} \sim 1500 \ cm^2/g$ specific surface areas were chosen to study HMX phase transition.

Whether HMX phase transition was absent or present was determined by the following methods:

-optical microscopy;
-temperature recording;
-IR-spectroscopy;
-x-ray analysis;
-pycnometric determination of HMX crystal density.

During these studies the HMX crystal habit and the changes in the main physical and chemical properties such as crystal density, thermal characteristics, molecular structure, phase composition were monitored. The tested HMX samples were thermally aged at the atmospheric pressure in thermostats of the measurement and computation complex (MCC) "Vulkan". They were aged at $160°C\pm0.1°$ for 1-7 days. After aging under the given conditions the HMX samples were removed and in about half an hour (HMX crystals were cooled to the room temperature) the samples were prepared to be further tested by physical and chemical methods.

STRUCTURAL STUDIES OF HMX

The HMX samples ($S_{sp} \sim 300 \ cm^2/g$) thermally aged at $160°C\pm0.1°$ for 1-7 days were tested by comparison with the original ones, for which purpose light microscopes MBS-9 were used. Photographs of the crystals were taken using MFN-5 microscopic photographic attachment.

In the course of thermal aging for 1-7 days the HMX crystals ($S_{sp} \sim 300 \ cm^2/g$) took on a yellowish-brown color. The more was the time of aging, the more intensively changed the color. Besides the color change, cracking and

turbidity of the crystals took place. This is shown in figure 1.

It has been found out that the more is the time of heating, the less is the portion of crystals preserving their original shape and the smaller are the fragments. It should be noted that crystal agglomerates produced after cracking are typical of the tested HMX samples. However, the produced agglomerates are not stable and they decompose after light pressing or treating with an alcoholic-water mixture (~ 95:5 vol.%).

The HMX crystals (S_{sp} ~ 1500 cm^2/g) having been thermally aged at 160°C for 1-4 days are identical with the original ones.

a   b

c   d

e
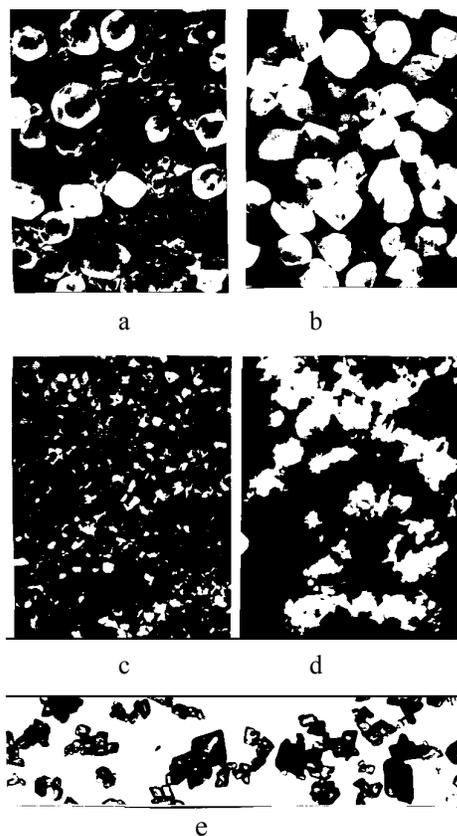
FIGURE. 1. S_{SP} ~ 300 CM^2/G (A-D) AND S_{SP} ~ 1500 CM^2/G (E) HMX CRYSTALS BEFORE AND AFTER HEATING AT 160°C (28^X): A – INITIAL; B – 1 DAY; C – 7 DAYS; D – AGGLOMERATES OF SMALL CRYSTALS IN 7 DAYS; E – 4 DAYS.

HMX DENSITY DETERMINATION WITH A PYCNOMETRIC METHOD

The densities of the tested HMX samples have been determined with a pycnometric method which is the most popular method for determining densities of powder solid materials. The error of the tested material density measured with this technique is no more ± 0.005 g/cm^3.

In the course of studies it was noted that the increased number of defects (such as cracks) in the thermally heated S_{sp} ~ 300 cm^2/g HMX caused a violent liberation of gas bubbles during its evacuation (as opposed to the initial product). No phenomenon of this kind was observed with S_{sp} ~ 1500 cm^2/g HMX. The experimental data are given in table 1.

TABLE 1. DENSITY OF HMX CRYSTALS.

Type, S_{sp}, cm^2/g	HMX characteristics	HE density, g/cm^3
300	Initial HE	1.899, 1.902, av. = 1.901
	HE after heating at 160°C, 4 days	1.835, 1.832, 1.834, av. = 1.834
1500	Initial HE	1.906, 1.904, av. = 1.905
	HE after heating at 160°C, 4 days	1.901, 1.902, av. = 1.902

From table 1 it can be seen that the density of S_{sp} ~ 300 cm^2/g HMX crystals after heating at 160°C for 4 days decreased to 1.834 g/cm^3 (the initial HMX density is 1.901 g/cm^3).

Such a great density change must testify to formation of new HMX phases. To support this suggestion, the HMX samples had to be analyzed using x-ray analysis and IR-spectroscopy specifying the phase composition of the tested material.

The density of $S_{sp} \sim 1500$ cm^2/g HMX crystals remained almost unchanged.

## STUDY OF THE HMX MOLECULAR STRUCTURE USING X-RAY ANALYSIS AND IR-SPECTROSCOPY

X-ray analysis of the HMX having been aged at 160°C for 1-7 days was made on the DRON-1 UM facility ~1 hour after heating using the characteristic copper anode radiation. The HMX crystals being in the initial state have a structure that is stable under normal β phase conditions. Figure 2 shows x-ray photographs of the crystals of the initial $S_{sp} \sim 300$ cm^2/g HMX and after its heating. From the matching diffraction lines it can be seen that thermal aging of the studied HMX samples results almost in no change in its structure. Similar x-ray patterns were also produced both for $S_{sp} \sim 300$ cm^2/g and 1500 cm^2/g HMX after its aging for 1, 3, 7 days.

Thus, no phase transformations in the tested HMX samples having been heated at 160°C for 1-7 days were detected by the x-ray analysis method.

Rate, Pulse/s
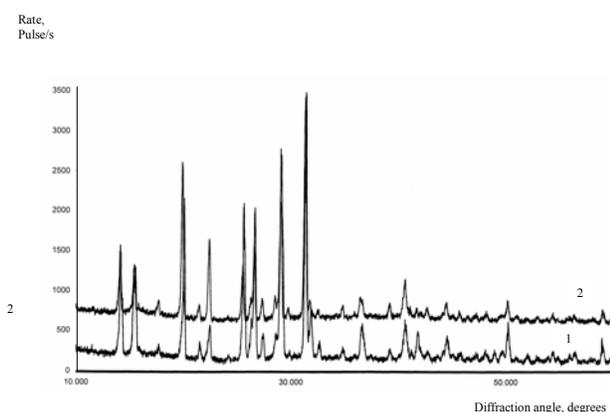
FIGURE 2. X-RAY PHOTOGRAPHS OF $S_{SP} \sim 300$ CM^2/G HMX BEFORE (1) AND AFTER 7-DAY HEATING (2) AT 160°C.

$S_{sp} \sim 300$ cm^2/g and 1500 cm^2/g HMX having been thermally aged for 1-7 days was studied with IR-spectroscopy method using $\varnothing$ 12 mm pressed samples of HMX and potassium bromide (KBr). All the samples were tested after ~1 hour of heating. The HE specimen in the sample made up 0.0005 g. The HMX IR spectra were taken with IKS-24 spectrophotometer over 2000-600 cm^{-1} range. After thermal aging the produced IR spectra of all HMX samples are identical to IR spectrum of the initial HMX and correspond to the β-phase HMX (figure 3).

Transmition, %

Wave numbers, sm^{-1}
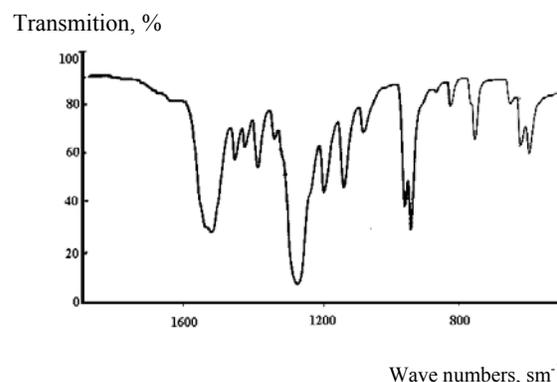
FIGURE 3. TYPICAL IR SPECTRUM OF β-PHASE HMX

Thus, no phase changes were revealed in the HMX samples tested by IR-spectroscopy and x-ray analysis methods after their heating at 160°C for 1-7 days. The results of X-ray analysis and IR-spectroscopy studies into the HMX samples show that the density change has resulted in no HMX phase change under the specified heating conditions.

STUDY OF HMX PHYSICAL AND CHEMICAL PROPERTIES

The HMX having been thermally aged for 1-7 days was tested by a thermographic (differential-thermal and thermogravimetric) method using a derivatograph of "Paulis" system. It has been found out that the thermal characteristics of all tested samples are almost no different from those of the initial HE: polymorphic transformation of HMX occurs over ~ 175-185°C temperature range, intensive decomposition is within ~ 250-290°C and the mass loss is ~ 95%. The derivatograms of S_{sp} ~ 300 cm^2/g HMX crystals before and after heating are shown in figure 4.

During the derivatograph tests two crucibles were used: an open crucible № 1 ($\varnothing$9, h = 12 mm) and a closed crucible № 2 ($\varnothing$13, h = 16 mm) (Figure 5). This was done to exclude probable ejection of the tested explosive fragments in the course of the experiment.
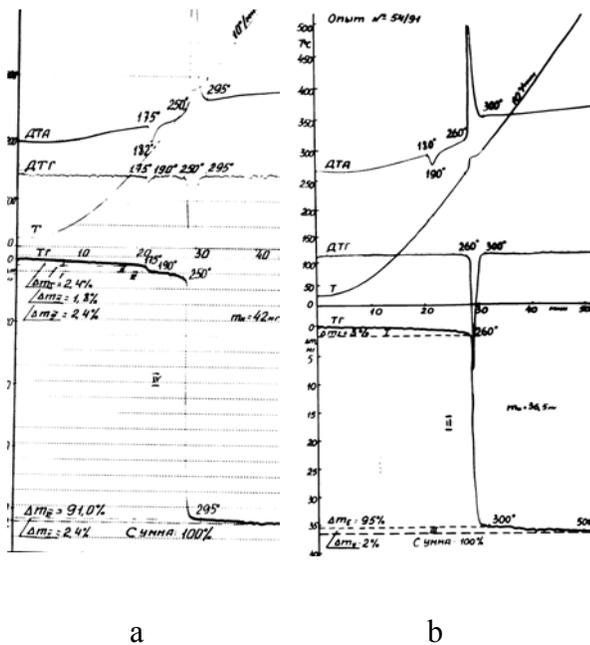

a   b

FIGURE. 4. DERIVATOGRAMS OF S_{SP} ~ 300 CM^2/G HMX CRYSTALS AFTER (A) AND BEFORE (B) HEATING.

Open crucible №1   Closed crucible №2

FIGURE 5. HOLDING CRUCIBLES.

During the tests with the open crucible the thermogram of S_{sp} ~ 300 cm^2/g HMX after its thermal aging shows an abrupt mass loss over 170-190°C temperature range: after aging for 2 days it makes up ~ 5%, 3 days - ~ 3%, 4 days - ~ 2%. The initial S_{sp} ~ 300 cm^2/g HMX as well as the S_{sp} ~ 1500 cm^2/g HMX before and after thermal aging have no abrupt mass loss of this kind. No abrupt mass loss was observed over the above temperature range of polymorphic transformation when experimenting in the closed crucible (№ 2). After processing the generated experimental data the authors have concluded that in case of a long thermal aging under the specified experimental conditions a part of gaseous thermal decomposition products remains "retained" in HMX crystals or in their fragments. Heating of HMX crystals during thermographic studies leads to structural rearrangement of crystals over the temperature range of polymorphic transformation. At the same time, the gas phase "retained" in the S_{sp} ~ 300 cm^2/g HMX crystals "gets free". This is accompanied by an abrupt mass loss (open crucible tests) testifying to ejection of HMX crystal fragments outside the crucible.

EVOLUTION OF GAS DURING HMX THERMAL DECOMPOSITION

The mass m of gas in the HE volume that is governed by HE thermal decomposition satisfies the following kinetic equation:

$$\frac{dm}{dt} = \left(\frac{dm}{dt}\right)_T + \left(\frac{dm}{dt}\right)_r \qquad (1)$$

where $\left(\dfrac{dm}{dt}\right)_r$ is the term describing the gas release from the volume;

$\left(\dfrac{dm}{dt}\right)_T$ is the term corresponding to gas production during HE thermal decomposition.

$$(dm/dt)_\tau = K_T^{ef}(m_0-m), \qquad (2)$$

where m_0 is the gas mass after HE complete decomposition (corresponds to the initial HE mass).

K_T^{ef} is the "effective" thermal decomposition constant.

$$(dm/dt)_r = (m_k-m)/\tau_r, \qquad (3)$$

where τ_3 is the specific temperature dependent time of gas releases from the HE volume, m_k is the gas mass "retained" in the HE volume (remaining asymptotically bound in the HE mass). Thus,

$$\frac{dm}{dt} = \left(\frac{dm}{dt}\right)_T + \frac{m_k-m}{\tau_r}. \qquad (4)$$

During thermal decomposition the gas mass in the volume is

$$(dm/dt)_T = m_0 \cdot K_T^{eff} \cdot e^{-K_T^{eff}\,t}. \qquad (5)$$

Thus, the kinetic equation takes the following form:

$$dm/dt = m_0 \cdot K_T^{eff} \cdot e^{-K_T^{eff}\,t\cdot}-m/\tau_r +m_k/\tau_r \qquad (6)$$

Solution of the kinetic equation (6) may be presented in the following form:

$$\delta(t)=$$
$$\frac{\gamma}{\gamma-1}(e^{-t/\tau_r} - e^{-K_T^{eff}t}) + \delta_k(1-e^{-t/\tau_r}), (7)$$

where $\delta = m(t)/m_0; \ \delta_K = m_k/m_0; \ \gamma = K_T^{eff}\tau_r$.

The gas mass produced during HMX thermal decomposition is

$$m_T(t) = m_0\cdot(1-e^{-K_T^{eff}\cdot t}). \qquad (8)$$

According to (7)–(8), the mass gas released from the volume is

$$m_r(t) = m_T(t) - m(t)$$

$$\delta_r=\frac{1-e^{-K_T^{eff}t} - \gamma(1-e^{-t/\tau_r})}{1-\gamma} - \delta_\kappa(1-e^{-t/\tau_r}). \qquad (9)$$

Let us consider the limiting cases.

1.   Slow gas release: $\gamma \cong \tau_r^{-1} << K_T^{eff}$, т.е. $\gamma = K_T^{eff}\tau_r >> 1$, then from (9) we have: $\delta_{r\approx}$
$$1-e^{-t/\tau_r} - \delta_\kappa(1-e^{-t/\tau_r}) = (1-\delta_\kappa)(1-e^{-t/\tau_r}). \qquad (10)$$

At $\tau_r \to \infty$ $\qquad \lim\limits_{\tau_3\to\infty} \delta_r(t)=0$ as it should be.

At $t \to \infty$ $(t >> \tau_r)$ we get from (10):

$$\lim \delta_r(t) = 1-\delta_k. \qquad (11)$$

This is the expected result: for long times the entire gas releases except for the "retained" gas. We consider the case of small times: $K_T^{eff}t << 1$ при $\gamma >> 1$.

In this case $K_T^{eff}t << 1$ при $\gamma >> 1$.

We have :
$$\frac{t}{\tau_3} = \frac{K_T^{eff}t}{K_T^{eff}\tau_r} = \frac{K_T^{eff}t}{\gamma} << 1.$$

We transform (9)

$$\delta_r(t) \approx \delta_r^{(0)}(t)\frac{t}{2\tau_r} - \delta_\kappa\frac{t}{\tau_r}, \qquad (15)$$

where $\delta_r^{(0)}(t) \approx K_T^{eff}t$ is the gas release in the absence of the gas phase delay (thermal decomposition).

This formula allows the parameters of the proceeding reactions to be estimated during HE thermal decomposition and "retention" of decomposition products.

2. Fast gas release: $\tau_r^{-1} >> K_T^{eff}$, т.е. $\gamma << 1$.
   From (9) we get:

$$\delta_r(t) = 1 - e^{-K_T^{eff} \cdot t} - \delta_\kappa (1 - e^{-t/\tau_r}) . \quad (16)$$

At $\dfrac{t}{\tau_r} >> 1$ $\delta_r(t) \approx 1 - e^{-K_T^{eff} \cdot t} - \delta_\kappa$.

At $\delta_\kappa << 1$ thermal decomposition takes place.

CONCLUSIONS

The studies were carried out to test the temperature and time effects produced on the possibility of polymorphic transition of $S_{sp} \sim$ 300 cm^2/g and 1500 cm^2/g HMX aged at 160°C for 1-7 days. They have shown that the tested HMX experiences no phase transformation.

After the studies the external appearance of HMX crystals and the changes in its main physical and chemical properties (crystal density, thermal characteristics, molecular structure, phase composition) were checked.

It has been found that heating at 160°C for 4 days leads to decrease in the density of $S_{sp} \sim$ 300 cm^2/g HMX crystals from 1.901 g/cm^3 to 1.834 g/cm^3. But this is not a criterion of HMX phase transformation.

Long-term thermal aging under the specified experimental conditions makes a part of gaseous thermal decomposition products remain "retained" in HMX crystals or their fragments. Further heating of HMX crystals during thermographic studies results in structural rearrangement of crystals over the temperature range of polymorphic transformation. At the same time, the gas phase "retained" in the $S_{sp} \sim$ 300 cm^2/g HMX crystals "gets free". This is accompanied by an abrupt mass loss (open crucible tests) testifying to ejection of HMX crystal fragments outside the crucible.

The formulas are given that allow the parameters of the proceeding reactions to be estimated during HE thermal decomposition and "retention" of decomposition products.

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