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THE DURATION PERIOD OF PROPELLANTS FOR CLASSICAL AND  
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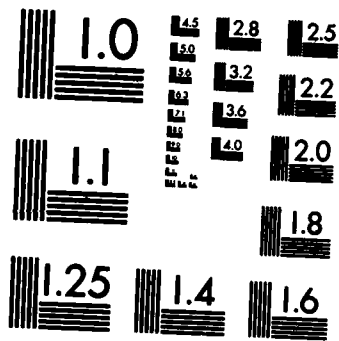
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# FOREIGN TECHNOLOGY DIVISION



THE DURATION PERIOD OF PROPELLANTS FOR CLASSICAL AND ROCKET ARMAMENT

by

M. Colakovic



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## THE DURATION PERIOD OF PROPELLANTS FOR CLASSICAL AND ROCKET ARMAMENT

M. Colakovic

A review is given of the achievements in the realm of forecasting the secure storage and use of solid propellants. Specific attention is given to rocket propellant, as the most critical element of the system. Its specific composition, form and grain size represent a suitable base for the development of a series of defects with catastrophic results during use.

### Introduction

Munitions must be considered as an element of an armament system which, in essence, consists of three basic components: metal, explosives and fuel. Since the elements which comprise the metal component are resistant to the problems of aging which stem from storage conditions (excepting the effects of corrosion), and the explosive component (brisance explosives) has a relatively large amount of energy from the activation of chemical decomposition, the greatest attention must be given to the propulsion component, the solid propellant, when the duration period of the munition is calculated.

The propellant should not be considered only as an organic material which combusts at a given moment, frees energy and fires the projectile. It is a complex, homogenous mixture of organic and inorganic material, specifically for a determined type of munitions. This specificity is mirrored in its composition, in its physical, chemical and ballistic properties, in its form and dimensions and in a series of other parameters, strictly defined for the particular projectile. The greatest number of limitations with regard to storage, transport and the use of munitions arises mainly from the complexity of the propellant as a heterogeneous material. In order to consider in detail these limitations and to influence them, one must keep in mind the complete system (when rockets are the subject) or only the munition (when dealing with classical armament),

in which this propellant is used. From these arise two basic types of propellant.

- I. Propellant for classical armament (classical propellant)
- II. Propellant for rockets (rocket propellant)

Such a division is justified not only for the examination of the propellants' usage period, but also with regard to its technology in view of the physical and ballistic properties, the dimensions of the propellant grain and even of its chemical composition.

The common characteristic of classical munition propellant is its form and dimensions. Different than those of rocket propellant, these grains are in the form of small platelets of various thicknesses, strips, rods and even tubes with one or more channels. Along with the chemical nature of the propellant, this characteristic plays a decisive role in calculating the security of storage. In connection with this, there also exists uniform conditions and instructions for monitoring the condition of the stocked munition on the basis of:

- the chemical,
- physical, and
- ballistic stability of the propellant.

#### 1. The chemical stability of classical and rocket propellant

The technical instructions for monitoring the stability of the propellant define only the monitoring of chemical stability, by which all propellant types would be protected from eventual self-ignition in storage. Accelerated tests are used at a high temperature in order to register the gaseous products as parameters of chemical decomposition (quantitatively or qualitatively) most often in the form of nitrous oxide. There is no proof that the results obtained can be extrapolated to storage conditions because the sample examined did not take into regard either the form or the dimension of the propellant or the vessel in which it was located. It also did not consider the storage temperature, which is the initiator of the chemical decomposition.

A significantly better test is to monitor the amount of stabilizer leftover in the propellant which was tested at high temperatures.

Since the complete control of the propellant's condition (as it is now organized) is aimed at preventing the propellant's self-ignition in the munition; that is to say, to anticipate when the quantity of heat released by decomposition would lead to self-combustion, the most competent test would, in a concrete system (munitions of various caliber or propellant block), measure the heat released by the propellant's decomposition and that which is exchanged with the surroundings during storage. Since, according to the law of heat exchange with surroundings in regard to the propellant's form and dimensions, there exists a minimum limit for the given conditions (storage temperature, the propellant's composition) beneath which self-ignition cannot occur. Hence, by a suitable mathematical model one can develop an expression which will connect this critical value with parameters dependent upon the propellant's properties and storage conditions. Such an expression [1] has the form:

$$D_{kr} = \sqrt{\frac{4\lambda RT^2 \delta}{\rho_0 E q_{Ta}}} \quad (1)$$

where:

- $D_{kr}$  - the critical diameter that is to say, the diameter of the propellant block (the thick web in the case of a cylindrical block, the munition's caliber or, generally speaking, the diameter of the vessel in which the small grained propellant is located);
- $\delta$  - the non-dimensional parameter which takes into regard the propellant's form;
- $\lambda$  - the propellant's conductivity temperature;
- $R$  - the gaseous constant;
- $\rho_0$  - the propellant's density;
- $T$  - the storage temperature;
- $E$  - the energy activated by the process of the propellant's chemical decomposition;
- $q_{Ta}$  - the amount of heat freed by the propellant's chemical decomposition at the storage temperature.

Other authors [2] after examining the propellant's physical, chemical and thermodynamic properties have also obtained similar expressions for  $D_{kr}$ . On the basis of the data from expression (1), the minimum time it takes for a quantity of heat sufficient to provoke the propellant's self-ignition can also be determined:



$$t_{min} = \frac{C}{A} \frac{RT^2}{E} \exp. \frac{E}{RT} \quad (2)$$

C - the propellant's specific heat

A - the constant which contains the speed of the accumulation of heat which is dependent upon the propellant's composition, form and dimension.

Current technology has created very precise instruments which can measure the heat of the decomposition even at significantly lower temperatures than those which the classic tests demand. A determined quantity of the heat from the propellants decomposition could serve also as a measure for the propellant's energy state. This would be one of the chief elements in deciding to disarm the munition in order to replace its propellant because of altered ballistic parameters.

Illustration 1 shows the schematic relation of the value of  $D_{KR}$  in mm to a temperature of  $71^{\circ}C$  and the largest caliber of a classical munition for some types of foreign produced propellant.

Table 1 gives the change of the caloric value in % for ten types of classical propellant storage conditions of 10g at  $20^{\circ}$  and  $30^{\circ}C$ .

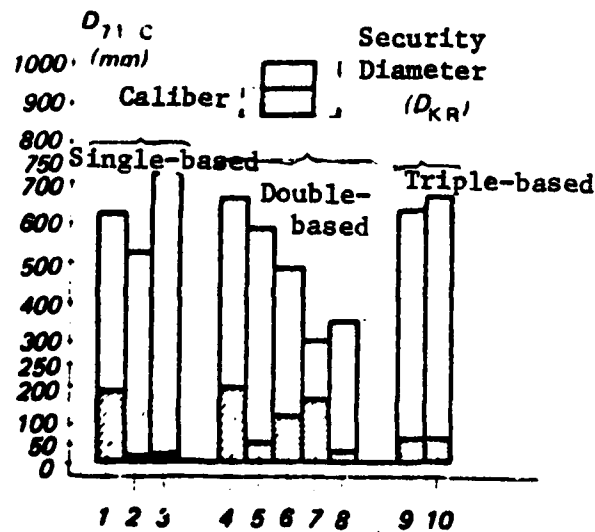


Illustration 1

From the results presented, it can be concluded that when one is dealing with classical munitions, no danger of self-ignition exists because the Dkr is significantly above the largest caliber. In regard to organizing the maintenance of munitions, danger exists when an unstable propellant is removed from the munition and placed in a container which remains in the magazine, standing for several months (and even years) while no decision is reached as to its further treatment. It is also necessary to give special attention to unactivated propellant stored as a war reserve.

Table 1

Propel- lant	10% stored	10% stored
	at 20°C	at 30°C
1 Single-	0.2	1.0
2 based	0.3	1.0
3	0.1	0.5
4 Double-	0.2	0.7
5 based	0.1	0.6
6	0.2	0.8
7	0.5	1.7
8	0.6	2.5
9 Triple-	0.2	0.7
10 based	0.1	0.7

When rocket propellant is in question with regard to the configuration and size of its web, it is possible that amassing of heat, sufficient for causing self-ignition comes much earlier than with classical propellant and the proposed test along with the determination of Dkr would be more desirable for the evaluation of its condition in regard to dangers of self-ignition. However, when the condition of the rocket propellant is evaluated with regard to the duration of its use, the stability of the physical changes in the propellant block is much more significant than the chemical stability.

## 2. Physical changes in the rocket propellant's block

The entire maintenance organization must aim at securing the longest possible usage "life" of a rocket system. By "life" of a system is meant:

- security during storage and transport, and
- security during usage.

The concept of security includes:

- the danger of self-ignition expressed through chemical stability;
- the danger of an eventual explosion during usage which can occur most often as the result of physical changes in the propellant during storage, and
- the danger of eventually missing the target because of changes in the propellant's ballistic characteristic.

With rocket propellant, as different from classical, the possibility is significantly more acute that all these changes will occur during storage, transport and use.

Experience shows that solid rocket propellant first becomes unusable because of physical defects (longitudinal and transverse cracks in the propellant block and in the inhibitor, the breaking off of the inhibitor from the propellant and the propellant from the motor, if the grain is bonded, the degradation of mechanical properties), than because of the reduction of its chemical stability. The causes of these defects are varied and numerous: the organization of the propellant block, charge in the motor, the maintenance conditions, the mutual low tolerance of individual components in the propellant's mass, irresponsible production procedures, chemical decomposition of individual components and the like.

2.1 The effect of the products of the propellant's chemical decomposition on the appearance of cracks in the propellant mass.

During storage, NC and NGL propellants decompose freeing gaseous products which accumulate in the propellant mass because of the porousness of it, the inhibitor and the rocket system (if the grains are bonded). This creates a pressure which can cause cracks of larger or smaller dimensions. Gaseous products can also arise in composite fuels because of the binder's reaction with the oxidizer. The time when these types of cracks appear can be anticipated [3]. In principle, cracks will occur when the pressure of the gaseous products of decomposition surpasses the value:

$$P = \frac{2\sigma}{1 + 2\varepsilon} \quad (2)$$

where:

- $\sigma$  - the intermittant hardness
- $\varepsilon$  - the intermittant elongation

The pressure can be measured directly by installing a capillary Hg manometer in the center of the propellant mass at a high temperature. Hence, data can rapidly be obtained about the speed of the formation of the products of decomposition. From the speed of gas formation and its diffusion through the propellant, Rosser [3] calculated  $P_{\max}$  which can arise in the propellant during its maintenance in stored munitions. The expression for the pressure of grains in a full cylinder form can be written as:

$$P_{\max} = \frac{Q \cdot d \cdot s^2}{4F} + 760 \text{ mm Hg} \quad (3)$$

- F - the speed of gas diffusion through the propellant
- Q - the speed of the gaseous products' development
- d - the propellant's density
- a - the charge's diameter

Wand [4], on the basis of Fick's law, developed a mathematical model for the calculation of the amount of pressure or the maximum concentration of propellant gases caused the products of decomposition in propellant masses of various forms. For strips:

$$C_{\max} = \frac{Q a^2}{2D} \quad (4)$$

- $C_{\max}$  - the maximum concentration of the gaseous products of decomposition,
- Q - the amount of gaseous products freed by decomposition,
- a - the strip's thickness,
- D - the diffusion constant.

When a full cylinder is in question:

$$C_{\max} = \frac{Q a^2}{4D} \quad (5)$$

- a - the cylinder's radius, and for a hollow cylinder:

$$C_{\max} = \frac{Q a^2}{4D} \left[ 1 - \left( 1 + \log \cdot \log (a \cdot b) \right) / \log \left( \frac{a}{b} \right) \right] \quad (6)$$

- b - the cylinder's internal diameter

For rocket fuel, when the propellant is attached to the chamber walls:

$$\ln a = \frac{1}{2} \ln \left( \frac{6 D \cdot C_{kr}}{A d} \right) + \frac{B - B'}{RT}$$

The influence of temperature on the occurrence of cracks in the propellant block is obvious. For a determined temperature there exists two critical diameters of the grain; that is to say, for the corresponding diameter of a grain there are two temperatures:

- the lower, beneath which the gaseous products of decomposition can run before the critical pressure is reached and cracks occur, and
- the upper temperature, above which diffusion can be ignored, and the cracks' occurrence period does not depend upon the size of the block

The propellant block's critical diameter, taking into regard the influence of temperature, can be calculated according to [4] as:

$$\ln a = \frac{1}{2} \ln \frac{6 D \cdot C_{kr}}{A d} + \frac{B - B'}{RT} \quad (3)$$

In one observed temperature range, the change  $C_{kr}$  is irrelevant and hence we can write that:

$$\frac{6 D C_{kr}}{A d} = K \quad K = a_{krit} \quad (9)$$

so that:

$$\ln a = 1/2 \ln K + 1/2 \frac{B - B'}{RT} \quad (10)$$

When, by the aid of equation (9), one can calculate the critical diameter for a temperature, then by aid of expression (10) that diameter can be determined also for another temperature.  $B-B'$  is determined experimentally from the difference of the quantity of gases arising from decomposition and those which exit through the grain by diffusion. The critical concentration of the gaseous products of the propellant's decomposition cannot be simply extrapolated from higher to lower temperatures. It depends on a series of factors upon which the influence of some can be seen from illustration 2. Here is given the relation of the concentration of gases in the propellant to the storage period.

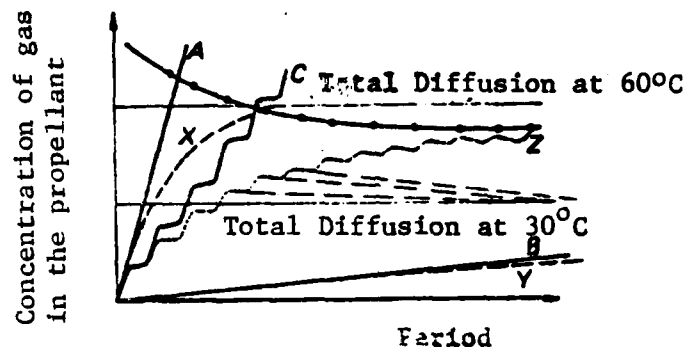


Illustration 2 - The accumulation of gases in the propellant block.

A - the azimuth which corresponds to the irrelevant diffusion at 60°C

B - the azimuth which corresponds to irrelevant diffusion at 30°C

C - irrelevant diffusion for the 60°/30° C cycle

x,y,z- the concentration when diffusion is not irrelevant

•—• - the critical pressure created by the gases

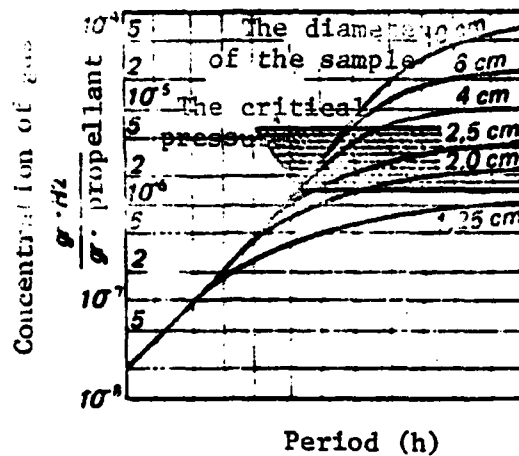


Illustration 3 - The change of the concentration of the gas in the propellant which is dependent upon the diameter's size at 46°C

The dependence is given in Illustration 3 of the calculated concentration of the gaseous products created by the propellant's decomposition upon its storage period at 46°C for propellant grains of a full cylindrical form with various diameters. The cross-hatched region represents the amount of the critical pressure for this propellant, calculated from formula (2). It is obvious that the pressure achieves its critical value significantly earlier in propellant blocks (grains) of larger dimensions.

## 2.2 The influence of technological factors upon the separation of the inhibitor and the creation of cracks in the propellant grain

Irresponsible technological production conditions for inhibited rocket propellant is most frequently manifested in the propellant's separation from the inhibitor and the longitudinal and transverse cracking of the inhibitor's mass.

The physical-chemical similarity of the propellant and inhibitor effects the possibility of the plasticizers migration from one center to another, its layering out in the contact strata and the formation of a permanent pressure in the propellant-inhibitor system.



The basic cause for the development of internal pressure in the propellant-inhibitor system is the contraction of the inhibitor during its hardening and use. During use, the contraction arises as a result of the change of the storage temperature, of the material destruction, of the molecular and super-molecular structural transformation, of the evaporation of the plasticizer and of the diffusion of gas and moisture.

With regard to the difficulty in experimentally determining the contraction level of the inhibitor (because of the possibility of the sliding of the still unhardened inhibitor mass in the propellant), the internal tension on the contact surface between the propellant and inhibitor is best determined by aid of the console method [5] and expression:

$$\sigma = \frac{E_1 \cdot f^3 \cdot h}{6 l^2 f_1 (f + f_1 - K)} + \frac{2\tau E_1 (F + f_1 - K)}{l^2} \quad (11)$$

where:

- $f$  and  $f_1$  - the thickness of the propellant sample in which the inhibitor is deposited and the thickness of the inhibitor,
- $E_1$  and  $E_2$  - the relaxation moduli of the propellant and inhibitor,
- $h$  - the elevation of the sample's free end,
- $l$  - the sample's length,
- $k$  - the position of the neutral line in the propellant-inhibition system

On the basis of the internal pressure determined in such a way, one can calculate the time when cracks develop under storage conditions [6].

$$\tau = \tau_0 \exp \frac{U_0 - \gamma \sigma}{RT} \quad (12)$$

- $\tau_0$  - constant  $\approx 10^{-13}$  sec,
- $U_0$  - the energy activated by the process of the separation of the propellant and inhibitor,
- $\gamma$  - the structural coefficient (the temporal sensitivity of the system's decomposition under a constant pressure),
- $R$  - the gaseous constant,
- $T$  - the experiments temperature,
- $\sigma$  - the constant pressure (internal pressure).

The internal tension can exist even in the propellant mass itself, especially when the propellant contains a large quantity of solid particles - filling material (as is the case for composite propellant). Then, internal pressure develops on the contact surface between the binder and particles of  $KC 10_4$ , Al and others. In this case, the pressure on the particle can be calculated as:

$$P = \frac{(m_c - am) \Delta TE_m}{(1 + M_c) + (1 + M_t) E_c / E_m} \quad (13)$$

and the radial and tangential pressure:

$$\sigma_r = -P (r/a)^2 \quad (14)$$

$$\sigma_t = P (r/a)^2 \quad (15)$$

where:

- $E_c$  and  $E_m$  - the module of elasticity of the hardened binder and filling material  
 $a_c$  and  $a_m$  - the coefficients of the linear temperature increase of the binder and filling material  
 $r, a$  - the external and internal diameter of the grain cylinder,  
 $\Delta T$  - the difference between the temperature of hardening (polymerization) and the temperature at which the pressure is determined,  
 $M_c$  and  $M_l$  - the Poisson number of the binder and filling material.

Besides those factors mentioned, there exists others which influence the physical stability of the solid rocket propellant and of the propellant-inhibitor system. Phenomena, such as the degradation of the propellant's mechanical properties during storage, the migration of NGL from the propellant into the inhibitor and basic polymers from the propellant and inhibitor as in the case of weak thermodynamic tolerance can also limit the usage period of a solid rocket propellant. The literature treats methods by which these changes can be observed and will not be dealt with separately.

### 2.3 Existing methods for controlling physical changes in the solid rocket propellant block.

We do not possess the data to work out the methods for controlling physical changes in the solid rocket propellant block which were claimed previously somewhere in the world, so that they would be accepted as official tests and introduced into the technology. As much as is known, in countries where this is demanded of the producer, simpler but much less secure tests are used, such as:

- the cycling of the propellant at extreme usage temperatures for a pre-determined time with defined climatic conditions;
- determining when cracks appear in the cube-shaped propellant sample, whose edge is 51 mm long. The cube is placed in Al-foil and maintained at  $80 \pm 0.5^\circ\text{C}$ . The development of cracks is controlled by X-rays at pre-determined time intervals. The critical size of the cube and the time when the crack appears

at the pre-determined temperature are obtained if a series of experiments are performed with cubes of various sizes.

- the level of the degradation of the propellant blocks' mechanical properties are calculated by measuring the reductions of contracted hardness and of the intermittent elongation in samples cut from the propellant grain, heated to various high temperatures, and by extrapolating the results for storage temperatures.
  
- the estimation of the compatibility of the propellant with ballistic modifiers is carried out so that the basic component of the propellant with a minimum stabilizer content is pulverized and combined with ballistic modifiers whose effect is pre-determined. This is then heated to 80°C in a vacuum until smoke appears, or until the mixture's temperature rises 2°C. If the time required for this phenomena is less than 20% of that obtained by testing the "standard" propellant, then that ballistic modifier should not be used.

## Conclusion

In order to best inspect the condition of a solid propellant with regard to its possible self-ignition, its secure use and ballistic stability, it is necessary to broaden control tests. Some tests which are already in use in some centers for the control of propellant block physical changes, could be immediately implemented. Those tests, however, by which the complex effects of the largest number of factors present in the concrete conditions of storage and use can be scientifically analyzed, remain in the realm of development as the theme of scientific work and research.

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