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FOREIGN TECHNOLOGY DIVISION

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by

Milos Colakovic

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EDITED TRANSLATION

(14) FTD-ID(RS)T-1044-80 (11) 5 Aug [redacted] 80

MICROFICHE NR: FTD-80-C-000952L

(6) THE SHELF LIFE OF FUELS WHICH ARE INTENDED
FOR CLASSICAL AND ROCKET ARMAMENTS

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English pages: 16 (21) Edited trans.

Source: Naucno-Tehnicki Pregled [redacted]
Nr. 2, 1979, [redacted]

Country of origin: (Yugoslavia) v29 n2 p18-25 1979, by
Translated by: LINGUISTICS SYSTEMS, INC.
F33657-78-D-0618
Nenad Popovic,
Requester: FTD/TQTR
Approved for public release, distribution unlimited.

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The Shelf Life of Fuels Which Are Intended for Classical and Rocket Armaments

by

Milos Colakovic

662.3 "401.7" (047)=861/362

A survey of achievements in the area of forecasting safe storage and exploitation of solid fuels. Particular attention is paid to rocket powder, which represents the most critical part of the system. Its specific composition, form, and grain size constitute convenient basis for the creation of defects which may bring about disastrous consequences during the exploitation process.

Introduction

Ammunition should be considered as an element of the armament system which, in essence, consists of three fundamental components: metallic, explosive, and fuel. Since the elements which constitute the metallic component are resistant to obsolescence originating from storage conditions (except for corrosion), and since the explosive component (brisance explosives) has a relatively high energy due to chemical decomposition activation, the greatest attention during the process of evaluating the shelf life of ammunition should be given to the fuel component, the powder.

The powder should not only be considered as an organic matter which burns at a given moment and conveys the energy which has been released, to the projectile. The powder is a complex homogeneous mixture of organic and inorganic matter, which is specific for any given sort of ammunition. This specificity is reflected in the composition of the powder, its physical, chemical and ballistic features, further its form, dimensions, and in a series of other parameters which are precisely defined for each given projectile. The greatest number of limitations regarding the transportation, storage and exploitation of the ammunition originates from the complexity of the powder which is a heterogeneous material. In order to be able to consider in greater detail such limitations and to do something about them, a thorough study of the entire system, either rocket or ammunition, is needed. From this statement two basic groups of powder logically follow:

I Powders for classical armaments (classical powders)
II. Rocket powders (powders for rockets).

The above division is justified both technologically and from the point of view of powder's useful life. In these respects it is important to analyze powder's physical and ballistic features, dimensions of powder grain and chemical composition.

The common characteristics of powders for classical ammunition are found in their form and dimensions. Unlike rocket powder, we have here powder in the form of very minute plates of varying thicknesses, fibers, sticks, or even minute pipes with one or more channels. Along with the chemical nature of the powder, this characteristic has a decisive role in the evaluation of storage safety. In connection with these, general and specific requirements and directions for the monitoring of the ammunition storage situation exist as follows:

- chemical
- physical, and
- ballistic stability of powder.

1. The chemical stability of classical and rocket powders

The technical directions for the monitoring of the powder stability only define the monitoring of the chemical stability through which all kinds of powders should be safeguarded from possible spontaneous combustion in the storage areas. Rapid tests are conducted at increased temperatures in order to find the parameters of the chemical destruction (both qualitatively and quantitatively), registering the gaseous byproducts, which most frequently appear in the form of nitric oxides. No proof exists to indicate that the results which were obtained, could be extrapolated to the storage conditions. The reason is that the examined sample does not take into consideration either the form, or the dimensions of the powder, of the container in which the powder is located and, evenmore, it overlooks the storage temperature which causes chemical destruction.

A test which monitors the quantities of the remaining stabilizer in the powder, which is tested at increased temperatures, is much better.

A complete supervision of the powder situation, as it is organized at present, is intended to prevent the spontaneous combustion of the powder in the ammunition. This means that by the time in which the powder would accumulate such a quantity of decomposition heat, which is able to cause the spontaneous combustion, must be determined. For this purpose the most reliable test would be the one that,in a given system(e.g. ammunition of various calibers, or powder in blocks), would measure and determine the heat which was created due to powder decomposition; to this should be added the heat which appeared during the storage as result of the heat exchange with the surrounding environment. According to the law of heat exchange with the environment, and with regard to the form and dimensions of the powder, a minimal diameter exists below which, under given conditions (such as temperature, storage, the powder composition), spontaneous combustion cannot occur. For this reason it is possible to apply the appropriate mathematical modelling and to arrive at a mathematical expression. The latter will connect this very critical quantity with the parameters which are determined by the powder characteristics, as well as with storage conditions. Such an expression (1) is as follows:

$$Dkr = \sqrt{\frac{4 \lambda R T^{2} \delta}{\rho_o^{E} q_{Ta}}}$$

where

Dkr = the critical diameter,namely, the diameter of the powder block, or the web thickness in the case of a cylindrical block, the size of the ammunition caliber, and the diameter of the container in which the small grain powder is located,

δ = the dimensional parameter which accounts for the powder form,

λ = the temperature conductivity of the powder,

R = the gas constant,

ρ_o = the powder density,

T = the storage temperature,

E = the energy of the activation process of the chemical powder destruction,

q_{Ta} = the quantity of heat which is released because of the chemical destruction of the powder at the storage temperature.

The other authors have also arrived at similar results for Dkr [2] on the basis of analyzing the physical, chemical and thermodynamic characteristics of the powder. On the basis of the data in expression (1), it is possible to also determine the minimal time within which such a quantity of heat, which will cause a spontaneous combustion will accumulate in the powder:

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

C = the specific warmth of the powder,

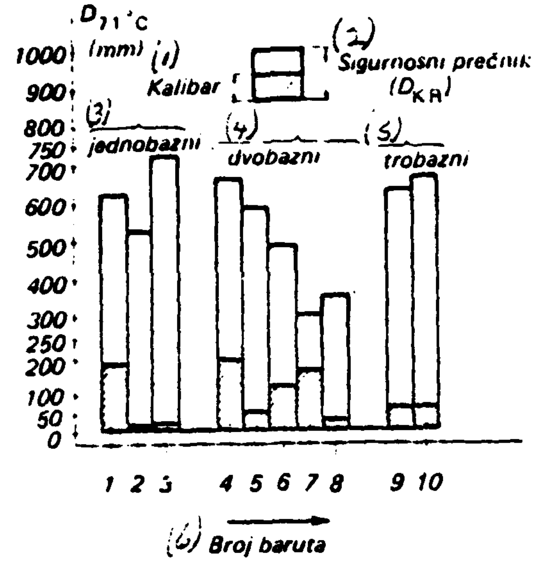
A = a constant which includes the velocity of heat accumulation, depending on the powder's composition, form and dimensions.

Contemporary technology today allows the use of highly accurate instruments with which the destruction temperature can be measured even at markedly lower temperatures than are required by classical tests. In this manner the determined quantity of heat, at which the powder decomposes, could also serve as the measure of the energy status of powder. This would be a decisive element for making the decision to take the powder out of the ammunition, on the basis of the ballistic parameters which were changed.

The relation of the value of Dkr in mm at a temperature of 71°C and the highest caliber of the classical ammunition for some kinds of powders manufactured abroad, is shown schematically in picture 1 [1].

The change of calorical value in % for ten kinds of classical powders, under conditions of storage for 10 years at 20 and 30°C, is given in table 1.

From the enclosed results it can be concluded that, when speaking about classical ammunition, there are no dangers from spontaneous comustion, since Dkr is substantially above the highest caliber. Concerning the organization of the



Picture 1.
Key: (1) Caliber; (2) Diameter; (3) 1-base; (4) 2-base; (5) 3-base; (6) No. of powder.

Table 1.

(1) Barut	(2) 10 g stokiranja na 20°C	(2) 10 g stokiranja na 30°C
1 (3) Jednobazni	0,2	1,0
2	0,3	1,0
3	0,1	0,6
4 (4) Dvobazni	0,2	0,7
5	0,1	0,6
6	0,2	0,8
7	0,5	1,7
8	0,6	2,5
9 (5) Trobazni	0,2	0,7
10	0,1	0,7

Key: (1) Powder; (2) Years storage time at; (3) 1-base; (4) 2-base; (5) 3-base

ammunition maintenance, there is the danger during the handling of the powder, which had been taken out of the ammunition because of its instability. Such unstable powder could be put, then, into buckets and wait in the storage area for months,if not years, until a decision would be made what to do with it. It is also necessary to pay full attention to the powder which is kept as the war reserve.

When we consider the rocket powders, and in respect to their configuration and web size, it is possible to have an accumulation of heat sufficient to lead to spontaneous combustion much earlier than is the case with classical powders. Thus, the proposed test would be more desirable in order to determine Dkr and to be able to evaluate the danger of spontaneous combustion. However, with regard to the life of the usable rocket powder, and in order to determine the powder's situation in addition to the chemical stability test, it is even more necessary to test the physical changes in the powder block.

2. The physical changes in the rocket powder block

The entire maintenance organization has the purpose of assuring as long a "life" as possible for the use of the rocket system. Under the term "life", the following should be understood:

- - safety during the storage and transport, and
- - safety during the use (exploitation).

The notion of safety includes:

- - the danger of spontaneous combustion as manifested through the chemical stability;
- - the danger of a possible explosion during the use (exploitation) which may appear mostly as a consequence of physical changes of the powder during its storage, and
- -- the possible danger that during the exploitation the target would not be hit due to changes of the ballistic characteristics of the powder.

As opposed to classical powders, in the case of rocket powders markedly higher possibilities that all of these changes will take place and sooner when stored, transported or exploited, do exist.

Experience also indicates that solid rocket fuel becomes unusable earlier due to physical defects. They are such as longitudinal and transversal cracks which are formed within the powder block and also on the inhibitor, then because the inhibitor peels from the powder or from the motor if the powder grain is bonded, or when the mechanical characteristics were degraded. Physical defects in general are a more important harmful cause than a reduction of powder's chemical stability. The causes of the aforementioned physical defects are many and of various kinds: the manner in which the powder block in the motor was filled, maintenance conditions, a low mutual tolerance of specific components in the powder mass, or because of inadequate manufacturing, of the chemical decomposition of the particular components, etc.

2.1. Consequences of the chemical powder decomposition and their influence on the appearance of cracks in the powder mass

During storage, NC and NGL powders do decompose and release gaseous products. These, in turn, because of the weak permeability of the powder, then because of the inhibitors and the rocket system itself (if the powder grain is bonded), accumulate in the powder mass pressures which can cause cracks of smaller and larger dimensions. Gaseous products can also be created in composite fuels due to the reaction of the adhesives with the oxidator. The time when such kinds of cracks can appear can be foreseen [3] . As a rule, the cracks appear when the pressure of the gaseous products of decomposition exceeds the value:

$$p = \frac{2\sigma}{1 + 2\epsilon} \qquad (2)$$

where

σ = the interruptory firmness of the powder,
ϵ = the interruptory elongation.

The pressure can be measured with a capillary Hg manometer directly positioned into the center of the powder mass and at an increased temperature. In this manner it is possible to arrive at data relating to the speed of the creation of decomposition products. Using the speed at which the gasses are formed, and the speed of their dilution through the powder, Rosser [3] has calculated P_max which can appear in the powder during storage in the stored ammunition. The expression for the pressure, when the grains are shaped as full cylinders, can be stated as follows:

$$P_{\mathbf{max}} = \frac{Q \, . \, d \, . \, a^2}{4F} + 760 \text{ mm Hg} \qquad (3)$$

F = the speed of the gas diffusion through the powder,
Q = the speed of the development of gaseous products,
d = the powder density,
a = the diameter of filling.

Wand [4] , on the basis of Fick's law, has developed a mathematical model for the calculation of the maximum pressure or of the maximum concentration of the powder gasses, which are created by the decomposition products within the powder mass in various forms. Thus, in the case of the fibers:

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

$C_{\mathbf{max}}$ = the maximal concentration of gaseous decomposition products,
Q = the quantity of gaseous decomposition products which are released,
a = the thickness of the fiber,
D = the difusion constant.

When we deal with powder in cylinder form:

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

a = the cylinder radius, and in the case of the hollow cylinders:

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

b = the inside cylinder's diameter.

In the case of rocket fuels, when the powder is glued to the chamber walls:

$$C_{\mathbf{max}} = \frac{Q \; a^2}{4D} \left[\log \exp \left(\frac{a}{b}\right)^2 - 1 + \frac{1}{\left(\frac{a}{b}\right)^2} - 1 \right. \qquad (7)$$

The influence of temperature on the creation of cracks in the powder block is evident. For a certain temperature two critical grain diameters exist, or rather, for a certain diameter two temperatures exist:

- the lower, below which gaseous decomposition products can flow out before reaching the critical pressure, and where the cracks do not appear,
- the higher temperature above which diffusion can be ignored and the time when the cracks appear is not dependent on the size of the powder block.

The critical diameter of the powder, taking into consideration the influence of the temperature, according to [4] can be calculated as:

$$Ina = \frac{1}{2} \frac{6\ D\ .\ Ckr}{Ad}\ e\ \frac{B - B'}{RT} \qquad (8)$$

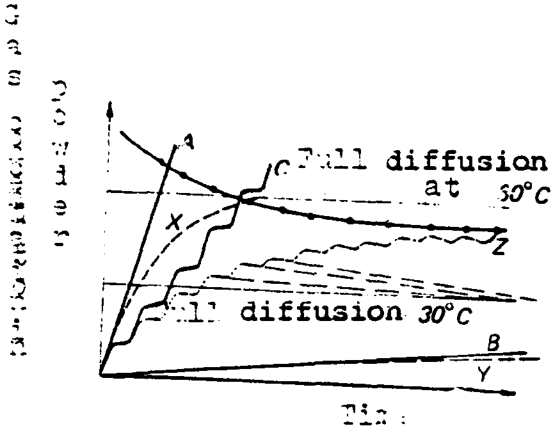
Within a considered temperature range, the change in Ckr can be neglected, and it may be written that:

$$\frac{6\ DC\ kr}{A\ d} = K \qquad K = a_{krit} \qquad (9)$$

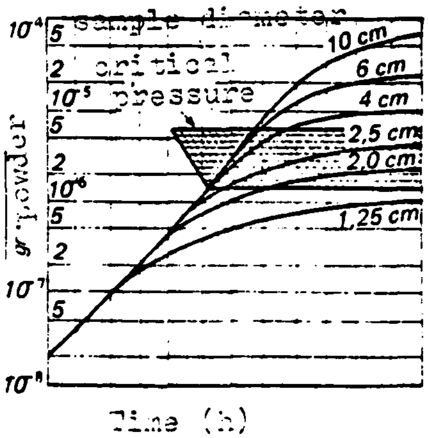
hence

$$Ina + \frac{1}{2}\ In\ K + \frac{1}{2}\ \frac{B-B'}{RT} \qquad (10)$$

When by using equation (9) the critical diameter for a given temperature is calculated, then by using expression (10) it is possible to also determine the diameter for other temperatures. B - B' is arrived at experimentally from the difference between the quantity of gasses which were formed by the decomposition process, and the quantity which exits by diffusion through the grain. The critical concentration of the gaseous powder decomposition products can simply be extrapollated from the higher temperature to the lower. The temperature depends on a series of factors. The influence of some of these factors can be seen in picture 2, in which the relation between the gas concentration in the powder and the length of time of the storage is given.



Pict.2.The gas accumulation in the powder block.



Pict.3.The gas concentration change in the powder depending on the diameter length at 46°C.

A=The asymptote which corresponds to the negligible diffusion at 60°C;

B=The asymptote which corresponds to the negligible diffusion at 30°C;

C=The negligible diffusion when cycling at 60/30°C;

x, y, z = the concentration when the diffusion is not negligible;

o-o-o- = the critical pressure created by the gasses.

Fig. 3 shows the dependence of the calculated concentration of the gaseous products which was created by the decomposition of the powder, since storing it at 46°C. The shaded area represents the value of the critical pressure for this powder, as calculated with formula (2). It is evident that the pressure, in the case of powder blocks (grain) with larger dimensions, arrives at its critical value much earlier.

2.2. The influence of technological factors in the peeling off of the inhibitors, and the creation of cracks both in in the inhibitor and in the powder grain

Inadequate technological conditions during the manufacturing of inhibited rocket powder is most often manifested in the form of the peeling off of the powder from the inhibitor, and both longitudinal and transverse bursting of the inhibiting mass.

The physical and chemical similarity of the powder and the inhibitor opens the possibility of plastificator migration from one medium into another. Furthermore it influences the stratification in the contacting layer between the powder and the inhibitor, and also it influences the formation of constant stresses in the powder-inhibitor system.

The main reason for the creation of the internal stresses at the contact area of the powder and inhibitor, is the inhibitor's contraction during the process of its solidification and use (exploitation). During exploitation the contraction is due to change in the storage temperature, to the material destruction, to the molecular and super-molecular structure reformation, to the plastificator vaporization, and to the gas and humidity diffusion.

Because of the difficulties in the experimental determination of the contraction degree of the inhibitor (because of the possibility of "through slippage" of still unsolidified inhibitor matter on the powder), the best way to determine the internal stresses in the contact surface between the powder and the inhibitor, is to apply the <u>console method</u> [5] and the expression:

$$\sigma = \frac{E_1 \cdot f_1^3 \cdot h}{6\, l^2 f_1 (f + f_1 - K)} + \frac{2h\, E_2\, (F + f_1 - K)}{l^2} \qquad (11)$$

where

f and f_1 = the thicknesses of the inhibitor and of the powder test-tube onto which the inhibitor is brought,

E_1 & E_2 = the powder and the inhibitor relaxation modules,

h = the elevation of the free end of the test-tube,

l = the test-tube length,

K = the neutral line position in the powder-inhibitor system.

On the basis of the thus determined internal stresses, it can be calculated the time within which the cracks will appear under the given storage conditions.[6].

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

τ_0 = the constant 10^{-13}sec,

U_0 = the energy of the activation process when the contact between powder and inhibitor is being torn,

γ = the structural coefficient(the time sensibility of the system destruction under a constant load),

R = the gas constant,

T = the experiment's temperature,

σ = the constant load (internal stresses).

Internal stresses can also exist in the powder mass itself, especially when the powder contains a large quantity of hard particles-fillers (as is the case with composite powder). Then the internal stresses appear on the contact surface between the bond and KC 10_4, Al and others. In this case the pressure on the particles can be calculated [7] according to"

$$P = \frac{(ac - am)\Delta TE\ m}{(1 + Mc) + (1 + M_1)\ Ec/Em} \qquad (13)$$

and the radial and tangential stresses:

$$\sigma r = - P\ (r/a)^2$$

$$\sigma t = P\ (r/a)^2$$

where

Ec & Em = the modules of elasticity of the solidified bond and filler,

a_c & a_m = the coefficient of the linear temperature extension of the bond and filler,

r, a = the outside and inside diameter of the grain cylinder,

ΔT = the difference between the temperature of the solidification (polymerization), and the temperature at which the pressure is determined,

Mc & M_1 = Poisson's number for the bond and filler.

From the values σ_r and σ_t, which were in this manner calculated, it is possible (12) to obtain the time which remains until the appearance of cracks or destruction by using this expression (12).

In addition to aforementioned, other factors which influence the physical stability of the rocket powders, as well as the powder-inhibitor system also exist. Cases, such as, for instance: the degradation of the mechanic characteristics of the powder during storage; the migration of NGL from powder into inhibitor on account of their low thermodynamic tolerance, may also limit the useful life of rocket powder. Since methods by which these changes can be monitored are published in literature, they will not be elaborated here.

2.3. Existing methods for controlling physical changes in the rocket powder block

We do not have data which would indicate that somewhere in the world the above outlined methods relating to the control of physical changes in rocket powder blocks have been so thoroughly developed as to be accepted and incorporated into official texts and technical specifications. So far as it is known, in those countries where the manufacturers have to meet such requirements, substantially simpler but also substantially less reliable tests are used, such as:

-The cycling of powder at extreme temperatures of exploitation, for a certain time and along with defined climatic conditions.

- The determination of time when cracks do appear in a sample of powder. This sample is usually in form of a cube whose sides are 51 mm; such a cube is wrapped into Al foil and is thermostated to 30± 0.5°C. At set time intervals the appearance of cracks is checked by applying X-rays. The crtical size of a cube, and the time when cracks appear at a given temperature, are arrived at by a series of experiments using cubes of different sizes.

- The degree of degradation of the mechanical characteristics of the powder block is determined by measuring the reduced stress firmness and the interruptible elongation in test-tubes which themselves are made of powder grains, which are checked at different increased temperature levels. The obtained results are then extrapollated to the storage temperatures.

- The evaluation of the compatibility of the powder with the ballistic modifiers is conducted as follows: the basic powder composition which has a minimal content of stabilizers ground and mixed with ballistic modifiers, whose influence is being investigated. All of this is then warmed up in a vac to 30°C, until it begins to smoke, or until the temperature of the mixture is increased by 2°C. If the obtained time of the mentioned changes is less for about 20% as compared to the time obtained by testing the "standard" powder, then this ballistic modifier must not be used.

Conclusion

To obtain a better insight into the powder status with regard to the spontaneous combustion, the safety of its use and its ballistic stability, it is necessary to broaden the control tests. Some tests which are elsewhwre being used for checking physical changes in a powder block could be accepted. There are conducted other tests researching the complex influences of numerous factors which are present during handling, storage and exploitation of powder. Such scientific effort will remain, at least for some time, a topic for research and development.

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Work received October 31, 1978.