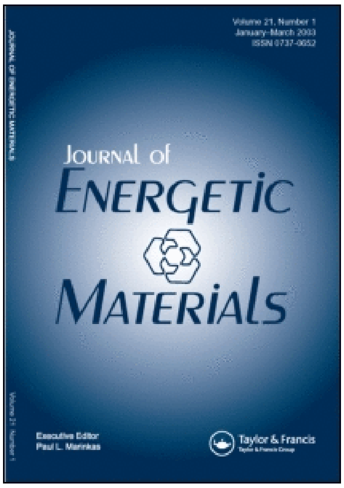

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A review of stability test methods for gun and mortar propellants, i: the chemistry of propellant ageing

L. Druet[a]; M. Asselin[a]
[a] Defence research establishment valcartier valcartier, QUEBEC, (CANADA)

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A REVIEW OF STABILITY TEST METHODS FOR GUN AND MORTAR PROPELLANTS, I: THE CHEMISTRY OF PROPELLANT AGEING

L. Druet and M. Asselin
DEFENCE RESEARCH ESTABLISHMENT
VALCARTIER
VALCARTIER, QUEBEC G0A 1R0 (CANADA)

ABSTRACT

Current methods for the prediction of the safe shelf life of gun and mortar propellants are evaluated. This is achieved in a four part approach. Firstly, the current picture of the chemical stability of gun propellants is presented. Secondly, the concepts of stability testing and artificial ageing are reviewed. Thirdly, the traditional and fourthly, the modern testing methods are discussed. In this way, it is possible to identify the reasons for replacing traditional with modern methods and to indicate the methods which would be most appropriate to implement in a country's stability surveillance program for its stored propellants.

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INTRODUCTION

Nitrocellulose(NC)-based gun and mortar propellants require routine chemical stability testing since the inherent instability of NC leads to self-ignition. A variety of testing procedures have been employed by different countries to monitor this instability and hence predict the safe shelf life of all the propellant batches. However, discrepancies have been found among the safe shelf life predictions of some of these methods, and the validity of the individual tests has been questioned.

Resultant investigations with modern analytical instrumentation have given a more accurate description of propellant degradation. This information has been useful in choosing the surveillance tests which best predict propellant instability. Thus the tests that were used routinely fifteen years ago have been replaced or at least supplemented in several countries by more modern methods whose superiority over the older or traditional tests is generally accepted.

For a country wanting to update its stability surveillance procedure but having limited resources and experience in the field, the choice must be made of the methods which are most appropriate. This article was written as an aid in such a situation as it describes the general status of the field of stability testing of gun and mortar propellants. Its principal objective is to give an overview of the chemistry and the methods which are being used and developed. Although some reference is made to the methods being employed by particular countries, the object has not been to summarize the methods used by each country but rather to indicate the state of development of each method.

In the following pages the discussion of stability testing is divided into four parts. The first part presents the current views regarding the chemistry of propellant ageing. The second part reviews the concepts of stability testing and artificial ageing. The third part presents the traditional methods which are used for stability surveillance and discusses the problems which have been encountered with some of these tests. The fourth part describes the recent analytical techniques which have been developed for stability investigations and assesses their feasibility for implementation in routine surveillance. The discussion concludes by indicating the general trends in the choice of optimum surveillance methods.

This report grew out of a Canadian need to improve the surveillance program for the gun and mortar propellants which are stored in Canadian Forces depots. Some of the traditional stability tests used in the depots were found to give inconsistent stability predictions. Explanations of the problem as well as better testing methods were sought. The report summarizes our findings. In so doing it sometimes chooses the current Canadian tests for illustrating specific points, but it is felt that this does not detract from the overall goal of the paper.

THE CHEMISTRY OF PROPELLANT AGEING

Outline

All types of gun and mortar propellants contain nitric esters ($RONO_2$) as their major component(s). Thus, in single-base propellants there is nitrocellulose (NC); in double-base propellants there is NC and a lesser quantity of nitroglycerine (NG), and in triple-base propellants there are significant amounts of NC, NG, and nitroguanidine (NQ). The NC is a polymeric nitric ester whereas NG is a simple, non-polymeric ester.

Under the conditions of long-term propellant storage, both types of nitric esters undergo a very slow, thermal decomposition. This may result in changes in propellant characteristics and a reduction of the chemical stability. Stabilizers are therefore added to the propellant formulations to help retard this decomposition and prolong the safe storage life of the propellant. It is the nitric ester decomposition processes and the role of the stabilizer in these which form a major part of the chemistry of propellant ageing.

The following paragraphs briefly present current views on this subject. The ideas which are briefly presented here have been discussed elsewhere in more detail [1-4]. Firstly, the decomposition of nitric esters is described. A scheme (Fig. 1) is presented to describe the chemical reactions of nitric esters and some related equilibria[2]. Then the changes occurring in NC-based propellants as a result of these reactions are considered. A modified reaction scheme (Fig. 2) is used to describe effects such as that of the stabilizer and of the diffusion of the evolved gases in the propellant[4]. Finally, various other factors which may affect decomposition in the propellant are considered.

Relevant Chemical Reactions

Figure 1 gives an overall picture of nitric ester decomposition. Nitric esters ($RONO_2$) are thermally unstable. They decompose in an exothermic manner via thermolysis, which is shown in eqs. 1 and 2[2]. Equation 1 shows the first step which involves breakage of the nitric ester bond; this causes denitration of $RONO_2$. Reaction products are nitrogen peroxide (NO_2) and the decomposed nitric ester RO·. Being free radicals, these are reactive species and they react immediately with nearby molecules of $RONO_2$.

The reactions which ensue are indicated by the series of arrows in eq. 2. Derivatives or deteriorated forms ($R'ONO_2$ where R′ is a shorter chain than R) of the starting nitric ester result and these products can react to produce other modified forms of $RONO_2$ along with carbon fragments such as oxalic acid ($C_2H_2O_4$). As well, a series of gaseous products is formed. These include nitric oxide (NO); nitrous oxide (N_2O), dinitrogen tetroxide (N_2O_4), nitrogen (N_2), hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO),

EQUATIONS FOR CHEMICAL DECOMPOSITION OF NITRIC ESTERS

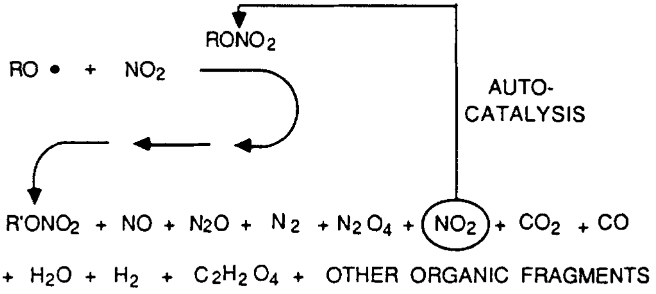
	THERMOLYSIS
EQ 1	$RONO_2 \longrightarrow RO\bullet + NO_2$
EQ 2	 $RONO_2$ $RO\bullet + NO_2$ AUTO-CATALYSIS $R'ONO_2 + NO + N_2O + N_2 + N_2O_4 + \boxed{NO_2} + CO_2 + CO$ $+ H_2O + H_2 + C_2H_2O_4 +$ OTHER ORGANIC FRAGMENTS
	OTHER REACTIONS
EQ 3	$2\,NO + O_2 \longrightarrow 2\,NO_2 \rightleftarrows N_2O_4$
EQ 4	$NO + NO_2 + H_2O \rightleftarrows 2\,HNO_2$
EQ 5	$3\,HNO_2 \rightleftarrows HNO_3 + H_2O + 2\,NO$
	HYDROLYSIS
EQ6	$RONO_2 + H_2O \overset{H^+}{\rightleftarrows} ROH + HNO_3$?

FIGURE 1

and water.

In addition to the processes represented by eqs. 1 and 2, there are subsequent reactions of or interactions among some of the reaction products. Thus as eq. 3 shows, NO is oxidized to NO_2 in the presence of oxygen and the NO_2 exists in a highly temperature-dependent equilibrium with its dimerized form N_2O_4. Equations 4 and 5 show that water, NO, and NO_2 are involved in equilibria with nitrous acid (HNO_2) and nitric acid (HNO_3). Thus the level of acidity may vary and this could affect the reaction scheme in several ways.

One noteworthy feature of NO_2 is its ability to catalyze thermolysis. As it accumulates, it accelerates further nitric ester decomposition. The result is that more heat is produced and the temperature in the propellant rises. This accelerating action of NO_2 is called autocatalysis. If it were left to occur in an uncontrolled fashion, then the rate of heat generation could eventually become higher than the rate of heat loss to the surroundings. The result would be a thermal explosion of the nitric ester after a certain induction period.

Water is present around the nitric ester as a result of thermolysis and it has been proposed that it can hydrolyse the ester[2]. This is indicated in eq. 6. However much more experimental evidence is required to substantiate this process and its overall effects.

Nitric Ester Decomposition in Propellants

When the nitric ester is considered as a component of the propellant, the reactions in Fig. 1 must be modified to account for other processes which affect decomposition under such conditions. The result is depicted in Fig. 2[4]. Here the general formula $RONO_2$ is used as well as that of nitrocellulose, since it is a major component of gun and mortar propellants. Both the interior of the propellant grains and the surrounding atmosphere are indicated since diffusion of evolved gases outward and diffusion of atmospheric oxygen into the grains are important factors here. The presence of stabilizer in the propellant is also critical because it inhibits the undesirable catalytic effect of NO_2. It reacts with NO_2 to form stabilizer derivatives.

Early in the propellant evolution, nitric ester decomposition has occurred only to a small extent. The possibility of reaction between the stabilizer and NO_2 is very low because of the high reactivity and low concentration of NO_2. As well, the stabilizer concentration is low relative to the concentration of $RONO_2$. The NO_2 reacts with other molecules of NC to give nitric oxide and carbon oxides. The small NO molecule can subsequently diffuse through the interior of the propellant and be released into the atmosphere or react with the stabilizer.

As further degradation of $RONO_2$ occurs, it is accompanied by continued local production of NO_2 and the secondary products as

CHEMICAL EVOLUTION OF NC-BASED PROPELLANTS[4]

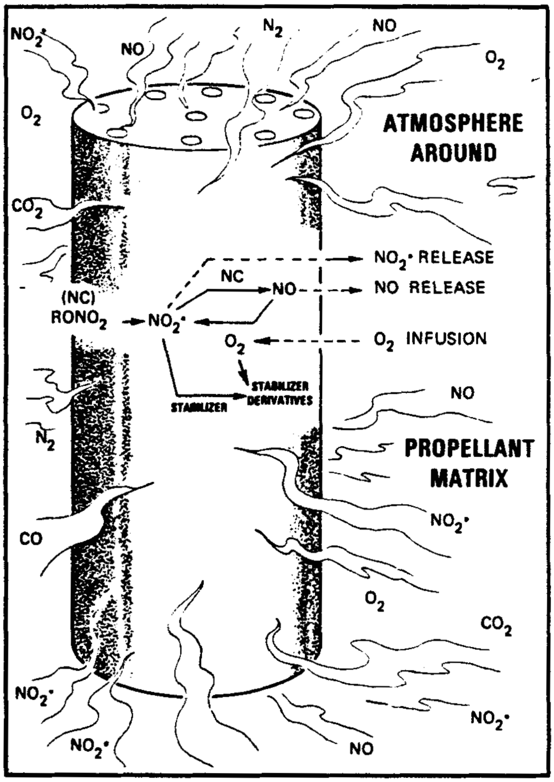


FIGURE 2

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well as an increased formation of stabilizer derivatives. As the NC molecular weight decrease small cracks begin to form. This facilitates diffusion of NO_2 and collision with a stabilizer molecule. Once the stabilizer is depleted, the propellant is no longer protected against the accelerating action of NO_2. The situation is dangerous and avoiding it is clearly essential. Stability tests are therefore performed to predict when this situation will arise so that the propellant can then be removed from the depots for disposal.

Other Factors Affecting Propellant Ageing

The succession of reactions described above can be affected considerably by several factors. Some of the more important environmental factors and effects of physical properties are mentioned in this section. The role of the stabilizer is considered in the following section.

Variations in physical properties of the propellant which can affect propellant ageing include its components and the method of formulation which was used. There can be variations in the distribution of nitric ester groups and in the degree of polymerization of the NC. Variations in the formulation method result in many differences such as porosity, degree of gelatinization[5], wall thickness of the propellant grains, and coating agents for the grains as deterrents and for glazing. Excellent discussions of these effects are available[1,2].

A recent study showed that calcium carbonate affects the chemical evolution of the propellant[6]. It may have been introduced inadvertently by the water used to wash the propellant or introduced during the processing. Its proposed effects were to change the concentration of NO_2 in the propellant, change the texture of the grains, or reduce the acidity.

Environmental factors are also important. As eq. 4 of Fig. 2 suggests, the water content of the propellant as well as the humidity of the storage conditions will affect the reaction scheme. Another example is a study which showed that the absence or presence of oxygen affects propellant samples packed in cartridges whose seals are airtight or leaky[7]. Sealed containers containing air slowly build up pressure of gaseous decomposition products that differ from those in the leaky containers. The rate of propellant decomposition also differs in the two cases.

Heat exchange is also very important. The second part of this article shows that temperatures for safe storage and for stability testing must be carefully chosen.

Stabilizers and Their Derivatives

The subject of stabilizers has long been an area of major interest in the field of propellant stability. The most common stabilizers are diphenylamine (DPA) for single-base gun propellants and ethyl centralite (EC) for double- and triple-base gun propellants. There have been many investigations of these stabilizers and of their derivatives which are formed from reaction of the stabilizer with the products of nitric ester decomposition. Early studies[9-14] dealt with identification of the DPA and EC derivatives as well as their preparation, proposed order of formation and stabilizing role in the propellant.

In later years improved techniques were utilised to give results which confirmed the earlier proposals[15-33] and added more information. For instance, a German study[34-35] resulted in separation and identification of the products from DPA and EC after storage of single- and double-base propellants, respectively, at temperatures between 60° and 95°C. The following 28 derivatives of DPA were identified:

> 2-nitro-; N-nitroso-; N,4-dinitroso-; N-nitroso-4-nitro-; 3-nitro-; 2,6-dinitro-; 2,4-dinitro-; N-nitroso-2,4-dinitro; 2,2'-dinitro-; 2,4,6-trinitro-; 2,4'-dinitro-; N-nitroso-2-nitro-; N-nitroso-4-4'-dinitro-; 4-nitroso-2-nitro-; 4-nitro-; 2,2',4,4'-tetranitroso-; N-nitroso-2,4'dinitro-; N-nitroso-2,2'-dinitro-; 2,2'4-trinitro-; N-nitroso-2,-2',4-trinitro-; N-nitroso-2,4,4'-trinitro-; 2,4,4'-trinitro-; 2,4,4',6-tetranitro-; 2,2',4,4'-tetranitro-; 2,2',4,4',6-pentanitro-; 4-nitroso-; 4,4'-dinitro-; 2,2',4,4',6,6'-hexanitro-diphenylamine, and picric acid.

Ethyl centralite gave the following 24 products:

> nitro-; 1,3-dinitro-; 1,3,5-trinitrobenzene; 2-nitro-; 4-nitro-; 2,4-dinitro-; ethyl-; 2-nitroethyl-; 4-nitroethyl-; 2,4-dinitroethyl-; 2,4,6-trinitroethyl-; N-2,4-6-tetranitroethyl-; N-nitrosoethyl-; N-nitroso-2-nitroethyl-; N-nitroso-4-nitroethylaniline; 2-nitro-; 4-nitro-; 2,4-dinitro-; 4,4-dinitro-; 2,2',4,4'-tetranitroethyl centralite; 4-nitro-; 2,4-dinitro-; 2,6-dinitro-; 2,4,6-trinitrophenol, and picric acid.

Similar results have been obtained by other workers.

In both cases an N-nitroso derivative and a mono-nitro derivative are among the first products to appear. With increased heating time there are increasing degrees of nitro substitution, from mono-nitro to dinitro to trinitro, etc. The overall scheme is complex.

Fewer compounds have been identified in single- and double-base propellants which have been stored for long periods at normal storage temperatures. A 1976 Swiss study[36] on an NC-based propellant manufactured in 1927 found DPA derivatives as follows: 2-nitro; 2,2'-; 2,4-; 2,4'-; 4,4'-dinitro; 2,2',4-; 2,4,4'-trinitro- and tetranitrodiphenylamine. Trace quantities of N-nitroso-4-nitro- and N-nitroso-4,4'-dinitrodiphenylamine were also detected. A 1979 UK study on a 15 year-old single base propellant revealed 0.77% DPA, 0.23% N-nitroso-DPA, 0.02% 2-nitro and 0.04% 4-nitrodiphenylamine[37]. Similar products were found in the same proportion when an NC-based propellant was heated at 65.5°C for about 24 days during the NATO Test.

Although the order of appearance of the derivatives has been known for many years, the kinetics of their formation and of the stabilizer reactions with nitrogen oxides are not well-known. Additional reactions of the stabilizer derivatives, especially as stabilizers in their own right, are important but are as yet incompletely studied under conditions which reflect their environment in the propellant. DPA has been shown to have better stabilizing ability then EC; however, the other factors discussed above must be considered in determining propellant stability. Thus well-gelatinized, double-base propellants (EC stabilized) often behave in a less hazardous manner than some single-base propellants (DPA stabilized) because of the better distribution of stabilizer in the former.

The stabilizer and its derivatives form a complex aspect of gun and mortar propellants. It is believed that the number and identity of these derivatives may vary with the propellant and with the conditions to which it has been subjected, such as changes in temperature, humidity, and gas confinement. A knowledge of these derivatives could indicate the state of evolution of the propellant. More will be said about this in the discussion of testing methods which follows.

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