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KINETIC METHODS APPLIED TO THE ASSESSMENT THE LIFE TIME OF ARTILLERY POWDERS

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Abstract: *An artillery powder undergoes slow exothermic decomposition because of their nature, even at moderate temperature. Nitrate esters and especially Nitrocellulose are not stable in nature. Add a certain amount of stabilizer material to the artillery powder to prevent a self - acceleration of its decomposition.*
Such a product, generally Diphenylamine or Centralite, reacts with nitrogen oxides evolving during the degradation and absorbs them. When it is fully consumed, there is some auto – ignition risks and then the powder is considered to be dangerous. So the predication of time when such a phenomenon happens would be much appreciated. Chemical kinetic methods have been proposed 20 years ago by Jack and Trenchant. Recent progress, especially in an analytical chemistry, allows us to re – examine the question.
Stability tests, now performed on artillery powder, give only and even not always an idea of real stability of the product which may be defined as the slowness of its decompositions. They do not allow assessing any life time value. Only Stan (60 days of artificial aging at 65.5 ^{o}C and spectro – photometric determination of stabilizer content decrease) assures a 5 years life time in normal storage conditions as positive.
All usual tests involve high temperatures and their results can not be easily connected with the real stability of powders. Moreover, the determination of life time of powder requires several experiments. It is possible to manufacture an artillery powder satisfying stability tests and, in fact, being instable. Therefore; there is a need to define a scientific method assessing the life time of an artillery powder.

NOMENCLATURES

G.C.	Gas chromatography
T.L.C.	Thin layer chromatography
DPA	Diphenylamine
NODPA	Nitrosodiphenylamine
NO_2DPA	Nitrodiphenylamine
k_1 , k_2	Rate constants
E_1 , E_2	Activation energy

KINETIC METHOD ASSESSING THE LIFE TIME

The parameter indicating an artillery powder state as regarding its stability is the residual stability content. The samples of gun powder are undergoing artificial ageing at various temperatures (100, 90, 80 and 60) ^{o}C. The residual stability content is determined on samples which have been regularly taken off the stove. $t^{1/2}$ is a time as the fifty percent of initial stabilizer has been consumed. In figure (1), using an extrapolation and assuming the decomposition process obeys an Arrhenius type law, it is possible to obtain $t^{1/2}$ at room temperature (30 ^{o}C). This time is the life time of an artillery powder. A final stability content of the fifty percent has been chosen in order to keep a safety margin [1].

The method of determining the stability content has a great influence on the result of life time assessment [2]. The evolution of stability content as a function of time is very different when determined by brominating, gas chromatography (G.C.) and thin layer chromatography (T.L.C.). In the case of diphenylamine stabilized gun powders, brominating conduces to an overall stability content, gas chromatography gives diphenylamine with about (50 %) of N-nitrosodiphenylamine and 2-dinitrodiphenylamine, only the thin layer chromatography gives DPA, MNODPA and other DPA derivatives. The assessment of ($t^{1/2}$) is very dependent on determination method (T.L.C.) conduces to a life time much shorter than (G.C.) and brominating.

Various single base propellants have been studied, several tests have been performed on sample underling accelerated aging in order to estimate the validity of usual tests and to investigate others. The tests performed (not systematically) on 6-nitrocellulose powders are the following:

1. Stability content determination using brominating, G.C. and T.L.C.
2. Vilely tests at temperature (108.5 ^{o}C).
3. Methyl violet paper tests at temperature (134.5 ^{o}C).
4. Vacuum test at temperature (100 ^{o}C).
5. Heat of combustion.
6. Determine the content of nitrocellulose nitrogen.

It is well known that one single test performed on a sample conduces only to a measurement of instantaneous artillery powder properties and not at all to a life time assessment. But, if it is a good indicator of the decomposition degree, it may be used in connection with the kinetic methods.

LIFE TIME ASSESSMENT

Numerous artificial agents have been performed (100, 90, 80 and 60) ^{o}C. They have shown that the degradation and stabilization process is not the same one at (60 ^{o}C) and at (100, 90, and 80) ^{o}C. At the beginning of decomposition, DPA content using (G.C.) decreases faster than expected and reaches a constant level of about (0.3 %), see figure (2). So the value obtained by extrapolation of ($t^{1/2}$) seems to be optimistic. On the contrary, the extrapolation of ($t^{1/2}$) seems to be pessimistic when (70 %) of initial stabilizer has been consumes. Therefore, the assessing of the life time is very dependent on the method of determining stability content and on the selection of critical stability content.

In a DPA stabilized artillery propellant, it may be approximately predict the evolution of DPA and N-NODPA content as a function of time. It is assumed that nitrocellulose decomposition process and stabilization mechanism are as follow the process of the degradation. Stabilization mechanism is:

$$Nitrogen \quad Oxidies + DPA \xrightarrow{K_1} N - NODPA$$

$$N - NODPA \xrightarrow{K_2} NO_2DPA$$

The real stabilization mechanism seems to be much more complex [3, 4].

The symbols (k_1) and (k_2) are rate constants and they are dependent on an artillery powder sample. The reaction is heterogeneous. Adjusting the values with experimental data, it may account for stabilization kinetics in this particular case. The constants (k_1) and (k_2) obey an Arrhenius Law with (E_1) and (E_2) activation energies. The energies (E_1) and (E_2) being different, it may explain that the mechanism is not the same in the whole range (30 - 100) °C.

*** 108.5 °C VILELY TEST**

It has been mainly performed on one propellant composition at various decomposition degrees. The results, figure (3), show that in this particular case, this test gives a good indication of residual stability content.

*** 134.5 °C METHYL VIOLET PAPER TEST**

On the same composition, the time to color change decreases when the stability content decreases. But below ratio of 0.4 % DPA), it remains at constant value of (40 min.) as shown in figure (4) .

*** VACUUM TEST (100 °C, 200 HOURS)**

The results of this test are not only dependent on residual stability content, but also on the temperature at which an artificial aging has been performed. The volume of a gas evolved from the artillery propellants containing either smoothing centrality or nitroglycerin tends to increase when residual DPA content falls below (0.1 % or 0.2 %). When the propellant contains none of these ingredients, the result seems to be independent of DPA content.

In addition, the long duration vacuum test have been performed at (100 °C) without centrality. The pressure, at the beginning, is a linear function of time and after about (300 hours), figure (5), the evolution becomes exponential. The relation:

$$P = a + b.t$$

Has a very good agreement with an experimental data. Where (b) is a linear function of residual DPA among and it increases with the decreasing of DPA content in a powder.

*** HEAT OF COMBUSTION**

The results are not significant except for the type of ball powders which containing nitroglycerin. The heat of combustion increases when DPA content in artillery powders falls below (0.2 % or 0.3 %).

CONCLUSIONS

This quick survey of stability tests and kinetics methods accessing the life time of single base propellant leads to the following conclusions:

(1) At present, there are no general and easy methods to perform the stability tests.

(2) What we call (the stability test) may only give an idea of decomposition degree of artillery powders at one moment.

(3) Several tests suggest the real critical stability content is about (0.2 % or 0.3 %) using G.C.

(4) The best indicator of gun powder decomposition is stability and derivatives contents, if determined by T.L.C.

(5) One way leading to realistic an evaluation of the life time would be using a modified (Jack and Tranchant) to stove a gun powder sample at moderate temperatures, for example; 65.5 °C and 55.5 °C and finally to observe the rate of stabilizer consumption using T.L.C. techniques.

REFERENCES

[1] Jack and Tranchant, "Powder laboratory center", Paris, 1964.
[2] J. May et, "The 3rd symposium of chemical problems connected with the stability of explosives", 1973.
[3] A. Palm, "Studies on reactions between nitrogen oxides and DPA compounds research institute of national defense", Sweden, 1983.
[4] N.J. Play, "Some relationships between the stability of nitrates and stability of propellants", Ministry of defense (U.K.), 1973.
[5] M.R. Hamad, "Shelf life prediction", Baghdad, 1996.