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A REVIEW OF STABILITY TEST METHODS FOR GUN AND MORTAR PROPELLANTS, II: STABILITY TESTING AND SURVEILLANCE*

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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.

STABILITY TESTING AND SURVEILLANCE

Outline

The speed of chemical decomposition of NC-based propellants is

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generally slow at the moderate temperatures used for normal storage (normally less than 40° or 50°C). The potential danger with these propellants is due to the autocatalytic effect of the evolved gases combined with the exothermicity of these reactions. Because propellants are not homogeneous, there exists a possibility that in some region the heat or gases evolved during decomposition may be prevented from being dissipated. The result will be a localized buildup of heat and gas pressure. In this region of the propellant there will be an increase in the rate of degradation. Once the temperature rises to approximately 170° or 180°C, self-ignition will occur.

Prevention of this hazardous situation is one of the main reasons why stored propellants are routinely surveyed. Tests of the chemical stability are performed and the results are used to predict the chemical shelf life, which is the time the propellant can be safely stored without risk of self-ignition. Such a prediction is often referred to as sentencing of the propellant. Every stability test is based upon some aspect of the phenomena indicated by Figs. 1 and 2. In addition, each test is designed so that it can be performed within a reasonable period of time. As will be seen in the following discussion, this requires artificial ageing of the propellant.

A large number of different surveillance tests have been developed for sentencing of gun and mortar propellants. Some have

EQUATIONS FOR CHEMICAL DECOMPOSITION OF NITRIC ESTERS

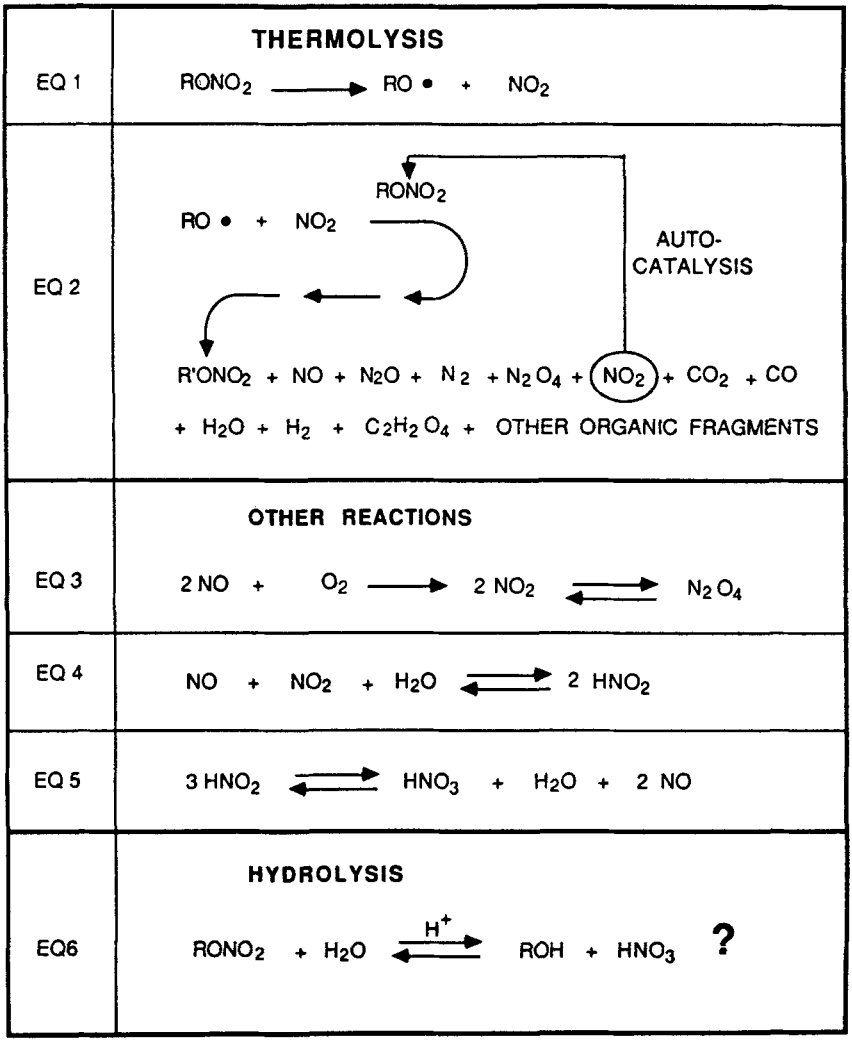

FIGURE 1

CHEMICAL EVOLUTION OF NC-BASED PROPELLANTS[4]

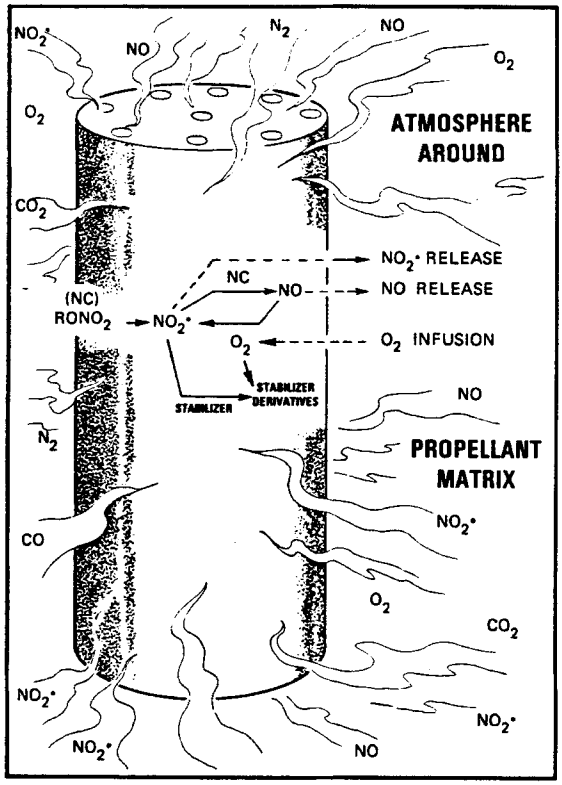

FIGURE 2

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been employed for many years and are referred to here as the traditional stability tests. Others date only from the past ten years and comprise a small group of recent analytical techniques. Different countries currently use various combinations of these traditional and modern tests in their surveillance programs. There are several recent methods which are highly regarded in many countries but have not been implemented in their surveillance programs. Nonetheless, the development of some of these methods is advanced and they are locally employed by propellant manufacturing plants. Stability tests must be performed in the plants to guarantee shelf lives of twenty or thirty years for new propellant lots. In this context the stability tests are actually acceptance tests.

Development and implementation of the most modern methods as acceptance tests is encouraged in the laboratories of propellant manufacturing plants because the most accurate and precise methods available are needed for optimum propellant production. In many other laboratories, investigations of modern methods are at a much earlier stage, perhaps because the need for the best methods is considered to be less urgent there. In these laboratories, further research on new methods is required before they can be implemented for stability testing on new lots or for surveillance of stored propellants.

The following chapters discuss the traditional stability tests and the modern test methods which are being used or developed.

Also included are current attitudes toward these tests as surveillance methods. For a better understanding of these attitudes, the concepts of artificial ageing and shelf life prediction are reviewed.

Shelf Life Prediction and Artificial Ageing

Propellants are normally stored at ambient temperatures (less than 40° or 50°C) where their decomposition is slow[2,38-41]. In fact, a few single-base propellants from World War I still exist and there are some double-base powders that are ten or twenty years old. Therefore, the physical and chemical changes occurring in these naturally aged propellants over a period of hours or a few days must be very small. Such changes would be undetectable by the test methods which were available fifteen years ago.

With the aim of achieving a reasonable testing time and test parameters whose variation is compatible with the precision of the instruments used to measure them, the traditional stability tests were designed for elevated temperatures. This procedure of heating the propellant at elevated temperatures is termed artificial or accelerated ageing. Artificial ageing of the propellant at elevated temperatures will increase the rate of decomposition and produce detectable changes in a shorter time. Stability tests are carried out on samples of artificially aged propellant and the results are used for a prediction of the shelf life at ambient temperatures.

Stability tests are based on the assumption that the rate of decomposition of the propellant may be estimated by monitoring the change in some chemical on physical property of the propellant. When a propellant becomes unstable, there are accompanying dramatic changes in the weight, the volume of gas evolved under vacuum, the exothermicity of combustion, the concentration of the stabilizer, and in many other properties. Studies indicate that the rates of change of these properties follow a similar temperature dependence as the rate of decomposition of gun and mortar propellants, although there are recognizable differences that depend on the property being measured.

Several years ago, a kinetic treatment was discussed for the estimation of the shelf life[38]. It involves artificial ageing of propellant samples at various elevated temperatures, e.g., 60°, 70°, 80°, 90° and 100°C, and measuring the change in the "free" stabilizer content of the propellant. Analysis of the data gives equations to predict the time for consumption of a given percentage, X%, of the stabilizer and a temperature coefficient to allow estimation of this time at the storage temperature.

The method was investigated and it was found that it depends on the technique used to monitor the stabilizer[39]. However, it forms a basic kinetic approach and all rigorous stability investigations involving shelf life predictions include similar kinetic considerations[4,7,29,35,36,38,39,40-52]. But the chemical equations used to treat the data may vary.

Many authors have assumed that the nitric esters in propellants, like esters in general, decompose at a rate which may be adequately described by the Arrhenius equation:

$$V = B\, e^{\frac{-E}{RT}}$$

Here V is the rate of nitric ester decomposition, E is the energy of activation for the decomposition, T is the temperature in degrees Kelvin, R is the ideal gas constant, and B is the frequency factor. This equation demonstrates the dependence of the reaction rate on the temperature.

Thus for gun and mortar propellants that contain NC and sometimes also NG as principal ingredients, the preceding discussion has shown how decomposition involves the thermolysis of the nitric esters as well as reactions of the stabilizer and its derivatives. Each process has been assumed to obey an equation of the Arrhenius type because the overall rate of propellant decomposition has been reported to roughly follow the Arrhenius law over limited temperature intervals. Therefore an activation energy E and a frequency factor B should be available for propellant decomposition. When the rate of propellant decomposition is estimated by the rate of stabilizer depletion, the calculated parameter is E^*, which is the apparent activation energy for stabilizer depletion. Studies of the stabilizer depletion rate conducted at several

temperatures from 50° to 120°C have shown that E^* depends on the nature of the propellant and is typically between 24 and 40 kcal mol^{-1}.

This proposed Arrhenius type of temperature dependence of the rate is not accepted by all investigators. Some feel that the assumption of overall Arrhenius behaviour in gun propellants is unacceptable[53]. Others feel that the quality of the data do not allow the distinction to be made between behaviour following the Arrhenius equation and behaviour following the Berthelot law[39].

Such kinetic studies at different temperatures provide the most exact and precise way that is available for predicting the safe shelf life. As well, they provide the most precise means of determining, for a given temperature, the remaining residual stabilizer content at which the onset of self-ignition will occur as a result of autocatalysis. When residual stabilizer content is measured, a determination is made of the time required for consumption of, for example, fifty percent of the initial stabilizer at each elevated temperature studied. Extrapolation then gives the time for fifty percent consumption at the storage temperature. This time is then used to predict the shelf life.

Problems arise with artificial ageing because sufficiently rapid routine tests require relatively high temperatures and do not allow time for the thorough kinetic studies described above. The actual stability test may involve a single test performed on one sample at an elevated temperature. The result is simply a measure

of the propellant properties at that instant and it is not a thorough lifetime assessment. But this measurement may be an acceptable indicator of the degree of decomposition.

Such acceptability will have been achieved if the sentencing criteria for the stability predictions of the test were drawn up using comparisons of the data at this elevated temperature with data obtained at lower temperatures. The lower temperatures must be sufficiently close to the propellant storage temperatures to ensure that no changes in ageing mechanism have occurred over this temperature range.

In situations where stability predictions are based on tests performed at an elevated temperature, the sentencing criteria usually have a safety margin incorporated into them to account for the extrapolation to the temperature of storage. This may make these criteria overly conservative to some extent so, of course, the predicted shelf life will be somewhat smaller than the maximum.

For example, in some stability tests based on stabilizer measurements, the useful or safe shelf life has been defined as the time for consumption of 50% of the stabilizer. This limit was chosen to account for the uncertainties in the extrapolation from elevated temperature and in the assumption of Arrhenius behaviour of the propellant's rate of decomposition. This definition incorporates a safety margin into the stability predictions.

Another problem is that the decomposition mechanism at elevated temperatures may not be the same as at normal storage

temperatures. In this case the extrapolation from elevated to ambient temperature may not be valid. Because of this, the temperature for a stability test should be chosen as a compromise so that it is high enough to produce a sufficient change in a measurable parameter but low enough so that it does not cause a change in the overall mechanism of propellant decomposition.

The highest acceptable temperature for artificial ageing is currently a controversial subject. However, it is generally accepted that for the most accurate assessment of storage life, a temperature as near as possible to the storage temperature should be chosen so that the extrapolation to a stability prediction of several years remains valid. As will be seen later in the discussion of weaknesses of the traditional stability tests, this is why there is a trend in some countries toward conducting the ageing at 40° or 50°C rather than at 65°C.

TRADITIONAL STABILITY TESTS

Tabulation of the Tests

The majority of the traditional stability tests for gun and mortar propellants are much the same as the tests used to determine the stability of pure nitric esters, in particular NC. Thus, samples from different lots are prepared, stored under ambient conditions, and periodically monitored. Most of the traditional surveillance methods involve periodic sampling and sentencing by stability testing. They are used in laboratories, magazines, and

propellant factories. Some methods involve measurement of evolved gas from a sample of artificially aged propellant, and others involve measurement of some physical characteristic of the solid propellant such as chemical stabilizer analysis, weight loss, or self-heating. The following paragraphs will summarize these tests and present current general opinions about them.

Table I defines most of the methods and gives an abbreviated description of each[9,36]. This table is relatively complete; it is missing only a few high-temperature tests which are no longer widely used. They include a heat test at 134.5°C, a manometric test at 135°C, and an American weight loss test at 115°C.

The first six tests (Nos. 1 to 6) in Table 1 are qualitative. Generally, a measurement is made of the time taken to evolve a known quantity of nitrogen oxides. If the time is considered too short in comparison with a reference propellant, then the propellent is termed unstable. To illustrate how these tests directly measure gas evolution, it is informative to consider one of them more closely, e.g., the Abel Heat Test, which is used in Canadian Forces depots.

For this test, samples are usually ground, then are heated at variuos temperatures (but typically 65.6°C) in a closed tube which contains a small rectangle of starch/iodide (KI) indicator paper. Nitrogen peroxide, NO_2, evolved from the propellant reacts with the paper to release iodine, which in turn produces a colouration in the paper. The time to produce a standard colour is

TABLE I

Traditional Stability Tests for Gun and Mortar Propellants

No.	Test	Temperature °C	Typical Time of Test	Description
1	Abel Heat	65.6	10–30 min.	KI-starch paper gives colour with nitrogen peroxide
2	Vieille	108.5 or 110 or 90	70 hours	Litmus paper changes colour with oxides of nitrogen
3	Methyl Violet	120 or 134.5	40 min.	Methyl violet paper changes colour with nitrogen peroxide (Times until red fumes form and explosion occurs also noted)
4	Silvered Vessel	80	500 hours	Time to pronounced exothermic reaction (2°C rise) is measured
5	80° Surveillance	80 (also 65, 100, 120, 135)	150 hours	Red or brown fumes seen; time for this decomposition is measured by KI Test before and after ageing
6	Lenze-Pleuss	78	90 days	Time is monitored until appearance of red fumes

TABLE I (Cont'd)

Traditional Stability Tests for Gun and Mortar Propellants

No.	Test	Temperature °C	Typical Time of Test	Description
7	Dutch	105	72 hours	Decomposition monitored by weight loss of sample
8	Small Vessel	100	5 days	Decomposition monitored by weight loss of sample
9	Will	135	4 hours	Reduce evolved oxides of nitrogen to nitrogen gas and measure the volume
10	Bergmann and Junk	132 (single-base) 120 (double-base)	2 hours	The quantity of acid product (calculated as No) evolved by the powder is deternined by dissolving evolved gases in water and titrating
11	Taliani	93.5 or 135	23 hours	Test is completed when the pressure in a constant volume apparatus reaches 100 mm above atmospheric
12	Colour	ambient	20 min.	Coloured stabilizer derivatives are measured by colorimetry
13	NATO	65.5	60 or 120 days	Loss in stabilizer is quantitatively determined by ultraviolet spectrophotometry

measured. If it is less than the prescribed time, then the sample is said to be unstable.

The next five tests (Nos. 7 to 11) in Table I also directly measure gas evolution. In this group, the quantity of gas produced after heating the propellant for a specific time is measured. If this quantity is considered excessive, the material is deemed unstable. These quantitative tests are more complex and time consuming than qualitative methods. Therefore, they are used less frequently in ammunition depots.

The last two entries (Nos. 12-13) in the table measure the amount of stabilizer consumed by reactions with nitrogen oxides. In this group are two methods which are currently used for routine surveillance of Canadian propellants; the Colour Test is qualitative while the NATO Test is quantitative. (The NATO test is also referred to as the STANAG 4117 test). The former involves dissolution of ground propellant samples in acetone. This test assumes that the intensity of the solution is due to the colour of the stabilizer derivatives. The intensity can be measured either by unaided visual determinations or by colorimetry. It is then related to the extent of ageing by comparing it to the intensities of standard solutions and criteria obtained from reference propellants.

The latter test (NATO Test) requires artificial ageing for 60 days at 65.5°C. The sample is then ground and refluxed in aqueous alcohol containing a strong base. The base hydrolyzes the

phthalate esters and converts nitrosated stabilizer derivatives, which have residual stabilizing properties, into forms which enable them to be determined[42]. Subsequently, the stabilizer and its derivatives are distilled off with steam. Analysis of this distillate by ultraviolet spectrophotometry gives the concentration of "effective stabilizer"[5]. This is the concentration of the stabilizer and all derivatives which contribute to the stabilization reaction. From this value a stability prediction can be made.

Problems with the Traditional Stability Tests

It is generally agreed that there are problems with the traditional stability tests. Some are general problems and apply to nearly all of the tests. Others are specific weaknesses which have been found with particular tests. The following examples illustrate some of the problems, which have prompted the development of modern surveillance methods.

Perhaps the most general problem which is evident from Table I is that heating at elevated temperatures is required in every case except the Colour Test. Even for the lowest temperature employed, i.e., 65.5°C, it is not known whether the reactions occurring are the same as those at ambient temperatures. To answer such a question would require a much greater understanding of propellant decomposition than what is presently possible. However, some laboratories which have been involved for many years in stability

testing still use elevated temperatures, including 65.6°, 75°, and 90°C in their studies. They argue that kinetic treatments of stability data obtained at these temperatures lead to extrapolated stability estimates which have been proven experimentally to be correct.

The tests which have been used extensively for routine surveillance have provided many results in which specific problems have been identified. Thus, one problem that was found with the silvered vessel test was that it was not possible to arrange samples which passed in some order of relative stability. This and other problems, along with the long test time (500 hours), have combined to result in this test being abandoned as a surveillance test in the United Kingdom[54].

The absolute stability predicted by the tests measuring decomposition by loss in weight of the heated propellant has been questioned. The weight loss may not be due to decomposition alone. There may be a significant contribution due to evaporation of nitroglycerine at these elevated temperatures.

A characteristic of the Abel Heat and Methyl Violet Tests is that they are specific for nitrogen peroxide (NO_2) but show no response to nitric oxide (NO)[56]. However, the discussion of Fig. 2 indicated the importance of NO in the chemical evolution of the propellant; therefore, a lack of specificity for NO suggests that there is a major weakness in the stability predictions of these tests. Other studies have shown that the meaning of the

color change of the methyl violet indicator paper is doubtful[57]. The Vieille Test uses litmus paper as the indicator and it has been found to give no valid information for propellants which contain nitroglycerine[57].

The results obtained with these tests which use indicators are dependant on the control, during the manufacture, of successive indicator lots, on the judgement of the operator, and on other factors which are not yet understood. Perhaps because of this, different countries have experienced different kinds of problems with a given test. For instance, in one country the Abel Heat Test gave several indications of poor stability when the propellant was stable[55]. The negative test result was attributed to changes in the solvent used for manufacturing or some other factor unrelated to the absolute stability. In a second country's surveillance program, the test indicated long-term stability for many single-base propellants after accelerated ageing whereas stabilizer analyzis showed that these propellants contained very low concentrations of the stabilizer and its derivatives[58]. A study by a third country indicated that the Abel Heat Test was reliable in evaluating their single-base propellants but unduly alarming in tests of stable double- and triple-base propellants[59].

In some cases, modifications of these surveillance tests have been developed and these have been found to offer some improvement. Thus the Abel Quick Test replaces the indicator paper in the Abel Heat Test with papers treated with alcoholic diphenylamine and

sulfuric acid; the result was found to be a greater potential for end point definition[59]. A modified Colour Test employs a spectrophotometer, calibrated at 440 nm, to remove any operator dependence associated with judging the colour intensity; this was found to be superior to visual methods not only for carrying out the test but also for the preparation and verification of the standard colour solutions which are employed in the test[60]. A modified NATO test employs a Markham semi-micro still, which is faster than the standard method and allows many stabilizer determinations to be made in a single day by one analyst[61,62].

However, these modified methods are disliked for the same reasons as the original tests. For instance, most of the shortcomings of the Abel Heat Test also apply to the Abel Quick Test. Both the Colour and NATO Tests measure the "effective stabilizer" content. Primary degradation products of the stabilizer are included. But the method of measurement does not account for the different extinction coefficients of these compounds. Thus these modified methods are not more popular than the original ones.

In summary, none of these traditional tests is completely acceptable. As has been seen, many of them involve experimental procedures which are no longer acceptable. In many cases there is probably a significant difference between the stability predictions which are given by these tests and the true or absolute chemical stability of the propellant samples being tested.

In spite of these shortcomings, the tests continue to be employed by many countries for routine surveillance. The recognized slowness to discard them is understandable. As they have been employed for many years, a considerable degree of experience with the test results has been acquired and it has been possible to interpret them in terms of the relative stabilities of different batches of a propellant. Another factor which has probably been important is that many of these tests are particularly suitable for a small test laboratory as they do not require complex procedures. This facilitated their implementation into surveillance programs involving large numbers of samples every year.

However, once a country experiences an unacceptable number of problems with the stability predictions of its traditional tests, it will be forced to look to other, more accurate methods. These new methods must be optimized for implementation into surveillance programs. They should also be economical alternatives to the older tests.

RECENT ANALYTICAL TECHNIQUES

The continuing search for improved stability tests has stimulated investigations using newer analytical methods. Within the last ten years, improved instrumentation has become available and has resulted in important studies via a variety of new, highly sensitive techniques. These include several chromatographic techniques, microcalorimetry, chemiluminescence, and mass spectrometry.

They involve determinations of the stabilizer and its derivatives. Their impact on the field of stability testing has been enormous. Some have already been adopted as surveillance methods in various countries. Some are used for stability studies in propellant factories. Others are still in the development stage. The following discussion will briefly consider these methods and illustrate their utility for surveillance.

Accepted Chromatographic Surveillance Techniques

Chromatographic techniques have been used mainly for determinations of the stabilizer and its derivatives. Three of the techniques have been developed and implemented in some countries' surveillance programs. These are thin-layer chromatography (TLC); gas-liquid chromatography, which is simply referred to as gas chromatography (GC), and high performance liquid chromatography (HPLC). The TLC technique has now been replaced by HPLC or GC, but the sample preparation techniques currently in use were developed for all three methods.

The oldest of the three methods is TLC, which effects separation of the stabilizer and its derivatives in a propellant extract. Early studies demonstrated the power of the method[12,13,16-18] and it was subsequently applied to many stability investigations. Researchers in various countries developed optimized solvent systems for the separations. These often required two, consecutive developments of the TLC plate for satisfactory separation of

derivatives differing significantly in polarity[20-25,34-36,63-70].

Apparatus was developed which enabled quantitative measurements by careful instrumental scanning of the TLC plates[16,36,68,69,71,72]. A modified method, called high performance thin-layer chromatography (HPTLC), was found to facilitate separations and quantitative determinations with high resolution and reproducibility[73,74]. As with TLC, the HPTLC apparatus is simple and commercially available[77].

The TLC and HPTLC methods give a more accurate picture of stabilizer consumption in aged propellants than is possible with the traditional methods. The experimental apparatus is one reason for this. Another is the improved methods of sample preparation which were investigated during the development of these two techniques. Traditional methods for the preparation of stabilizer extracts, such as the reflux in alcoholic base and the subsequent steam distillation used in the NATO test, were considered too harsh for the reasons cited earlier. Extensive studies of sample preparation techniques began with the TLC studies. They continued with and were equally applicable to the other chromatographic studies. Because of their fundamental importance, they will be summarized at the end of this section.

A TLC technique was implemented in one country's surveillance program[65,69,78,79]. Thus Sweden employed densitometers to automatically read and register ten thin-layer chromatograms in

succession. However, the TLC technique has now been replaced in Sweden by HPLC, which is more sensitive. The superior sensitivity of HPLC and GC is a major reason for the development of surveillance programs which incorporate these methods.

While GC has been used to study the gases evolved from aged propellants[80,81], its major application in the field of stability testing has been for quantitative separation of the stabilizer and its derivatives in propellant extracts. An early application was in the United Kingdom's surveillance procedure called the Woolwich Test. In this test, propellant samples are heated at 80°C for three weeks before their residual stabilizer content is determined by GC[59].

Since that time extensive research has resulted in optimized GC methods for stability studies[29,82]. The methods boast both high reproducibility and detection limits as well as good resolving power and the possibility for full automation. A limitation is the inability to separate diphenylamine and its main derivative, N-nitroso-diphenylamine, which is thermally decomposed wholly or partially into diphenylamine in the inlet port of the gas chromatograph.

For some applications, this problem has been resolved by derivatizing the diphenylamine prior to GC analysis[82]. But the derivation procedure is relatively long and complicated and the other popular chromatographic procedure, HPLC, does not have this problem because of its lower operating temperatures. It is perhaps due to

this that already developed GC methods are being used for surveillance (although in conjunction with HPLC) in only one country[83,84]. Many countries which are presently developing new surveillance methods have opted for HPLC.

The quality of HPLC columns which have become available in the last ten years in very high. As a result, the HPLC method is currently under the most widespread development of all methods for implementation in stability surveillance programs[46,84-87]. Other laboratories with experience in propellant stability have extensively used HPLC[27,29,30,37,46,73,89-91]. The method is rapid and offers the same performance capabilities as GC[29].

Experimental procedures vary. Both normal and reverse phase columns have been exploited. Ultraviolet spectroscopy has generally been the preferred detection method but electrochemistry has been shown to be a novel and feasible alternative[92-94]. One of the most important variables has been the method used for sample preparation.

To avoid high temperatures, mild methods of sample preparation were sought. Three of them involve extractions of the stabilizer and its derivatives into methylene chloride. One investigation concluded by suggesting that extraction could be accomplished by shaking the propellant in methylene chloride for 2 to 4 hours with a mechanical shaker[65]. A second accepted method is extracting by stirring or shaking the propellant and methylene chloride for 16 hours at ambient temperature[36,65,69,82]. In a third procedure

the stabilizer and its derivatives are extracted by refluxing in methylene chloride[49]; an extractor is now available to perform the same extraction in 40–60 minutes[28].

These are several other mild methods which are not based on extraction with methylene chloride. One involves preliminary overnight agitation of the propellant at room temperature, in a darkened room, with a mixture of 98% 1,2-dichloroethane and 2% THF, filtration of the supernatant liquid, and immediate analysis[95,96]. Another involves the softening of the cut-up propellant in methanol for various periods of time, followed by homogenizing with a laboratory homogenizer[86]. A third involves prior agitation for 15 minutes using a small propellant sample in a 50% acetonitrile/water solution and an ultrasonic micro tip, and subsequent sample filtration[87]. A fourth method involves use of an ultrasonic bath to dissolve the ground propellant in a solution of four solvents[27]. The two final documented methods involve precipitation of NC from the extract before chromatographic analysis: after total dissolution of the propellant in either acetone or acetonitrile, the NC is precipitated by addition of water to the acetone or by addition of a dilute $CaCl_2$ solution (~2%) to the acetonitrile[46,89].

Concentration Profiles of Propellant Extracts

These three chromatographic techniques have been used to construct concentration profiles for the stabilizer and its

derivatives in propellant samples of varying degrees of decomposition. The samples are obtained by artificially ageing for different times. Figure 3 illustrates this for samples of a Swiss double-base propellant, which was stabilized with EC. The heating was at 90°C and the evaluation of EC and its nine major derivatives was measured by HPLC[73].

Once obtained, concentration profiles must be correlated with propellant stability. Early studies suggested that naturally aged propellants near autocatalysis and artificially aged propellants near autocatalysis have similar concentrations of stabilizer and its derivatives[24]. They also suggested that the transformation rate of the stabilizer and its derivatives at elevated temperatures might be used to judge the safe shelf life of the propellant[68,82].

Some procedures which have been developed to predict the shelf life of propellants are based on reaction kinetics of the stabilizer during storage at elevated temperatures. In others, concentrations of the stabilizer and its principal derivatives in an extract of the propellant sample are used[83,84]. Both methods are adaptable for use in surveillance programs.

Viscosimetry and Gel Permeation Chromatography

The three chromatographic methods of HPLC, GC, and TLC measure concentrations of the stabilizer and its derivatives in aged propellants. They are therefore indirect measures of nitric ester

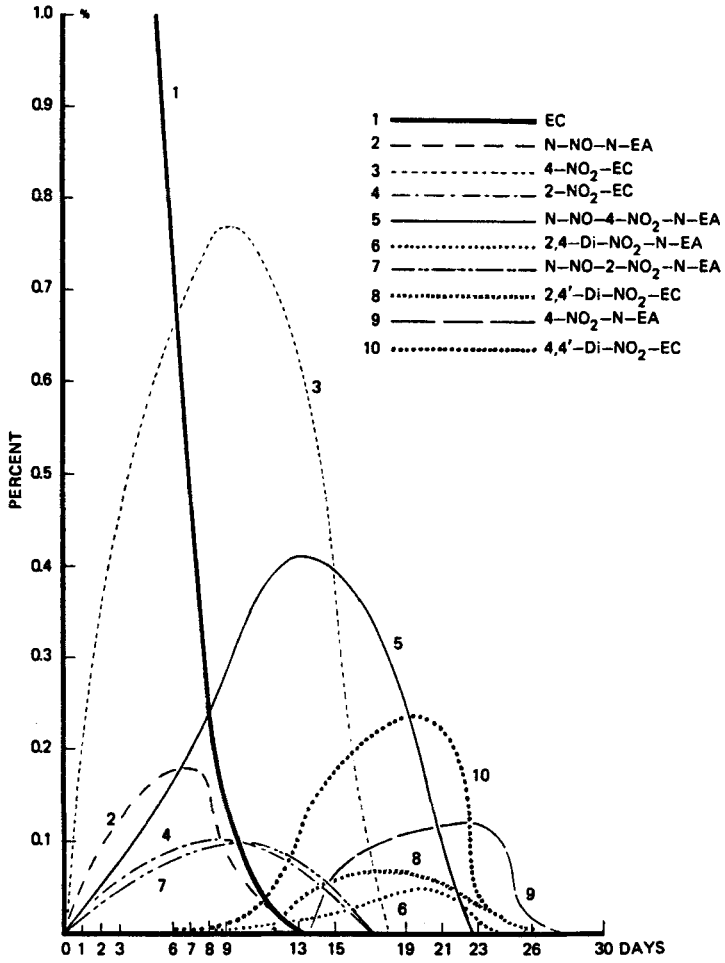

FIGURE 3

Concentration profile for ethyl centralite and its nine major decomposition products in Swiss propellant 5700 Ws heated at 90°C. Reprinted from Ref. 36 with permission. Copyright 1980 Sektionen för Detonik och Förbränning, Sundbyberg.

decomposition. More direct measures of NC decomposition can be obtained by viscosimetry and gel permeation chromatography (GPC). These methods are used to estimate the extent of breaking of the NC chains in aged propellants by measurements of the changes in molecular weight.

Viscosity measurements made on propellant samples at the time of production give information about the average size of the NC molecules in these reference samples. During later inspections of aged propellants, viscosity measurements are compared with reference values and stability estimates are made. This method has been incorporated into the Swedish surveillance program[65,78,79].

When GPC was applied to measure the molecular weight distribution of aged NC-based propellants, the results indicated that the method not only yields information about the chemical stability of the propellant. In addition, the changes in molecular weight distribution with propellant ageing appear to be related to the changes in ballistic properties of the propellants[44,47-49,52]. A correlation between chemical and ballistic properties has great potential application. However, although GPC is being used in a qualifying procedure during propellant manufacture, it is not being used in any country's surveillance program.

Microcalorimetry and Other Thermal Techniques

A completely different technique which has sparked considerable

interest in the last ten years is microcalorimetry[97]. In this branch of reaction calorimetry, very sensitive, commmercially available instruments have been specially designed for studying slow decomposition processes on small quantities of sample. In isothermal instruments, which are those most commonly used for stability work, the heat evolved in exothermic processes like nitric ester decomposition is transported out of the calorimeter vessel and measured. Thus the values obtained by this technique should directly reflect the chemical evolution of the propellant sample.

Methods have been developed by which the temperature distribution as a function of time can be calculated with a stored propellant mass; the calculation method has been verified by experiment[45,98-104]. Studies have also been made to demonstrate some of the experimental factors which influence the heat generated by the propellant under these conditions[47,105-110]. One result of the work was the implementation of an acceptance test based upon microcalorimetric measurements on new Dutch propellants[32,33,111]. Another outcome was the implementation of a microcalorimetric method into the French surveillance program. It is used for propellants which do not pass the primary stability test, which requires determination of stabilizer content by GC[83,84]. The method has also been incorporated recently into the Swedish surveillance program[112].

Several other thermal techniques have been applied to studies

of propellant stability. One is the coupled method of thermogravimetric analysis (TGA) plus differential thermal analysis (DTA), or DTA/TGA. However it has been found that this method distinguishes stable and unstable propellants much less clearly than the microcalorimetric method[113]. Another method is differential scanning calorimetry (DSC) which, like DTA/TGA, has not been sufficiently developed for surveillance applications[114]. Recently, the vacuum stability test has been used in conjunction with HPLC stabilizer measurements to follow the rate of formation of gaseous decomposition products[115,116].

Chemiluminescence

Another recent technique which is very useful for stability studies is the chemiluminescence NO_x analyzer[56]. It is sensitive and specific, allowing the determination of both NO and NO_2•. With it, the evolution of nitrogen oxides during propellant decomposition can be monitored continuously at moderate temperatures which are close to those for normal storage.

The method has been shown to be useful for studying several aspects of propellant stability such as decomposition rates of nitric esters at different temperatures; the influence of the stabilizer, different propellant ingredients and other materials on the decomposition; and differences in single-, double-, and triple-base propellants. It has been shown that chemiluminescence is an important supplement to stability information from other stability

tests[8,117-124]. However the method has not yet been developed for surveillance.

Other Methods

There are a few other techniques which have been used for stability studies but these have not received widespread application as testing methods. Examples are the methods of flowing afterglow spectroscopy[125] and electron spin resonance spectroscopy[126]. Mass spectrometry (MS) has been used to identify the gases causing cracking in propellants[127] and to study stabilizer derivatives. For the latter work, it has been used alone[128] and in a coupled mode, with either GC[129] or HPLC[75].

SUMMARY AND CONCLUSIONS

This report has attempted to describe and assess the test methods which are available for surveillance of propellant stability. To do this, the current picture of chemical stability and ageing of gun and mortar propellants was described. It was noted that increased understanding of these ageing phenomena has contributed to an evolution in attitudes toward the test methods. In many countries, traditional tests are becoming widely supplemented or replaced by modern techniques for stability studies. Also, several countries are now relying to an increasing extent on the newer methods for routine surveillance.

The principal limitation of the traditional tests is that many require accelerated ageing by heating at temperatures which are unacceptably high. With such procedures it is questionable whether the phenomena occurring in the propellant are the same as those which take place when the propellant is aged naturally. Thus there is a trend toward abandoning these tests and developing others in which little or no heating at elevated temperatures is required for sample preparation.

Among the traditional tests, only the Colour Test does not require accelerated ageing and an improved measuring technique is available. But, like the other tests, the accuracy of its predictions is limited. Of the remaining traditional tests, the NATO test requires heating at the lowest temperature, viz., 65.5°C, and this is considered by many to be too high. Other undesirable features of these older methods include some of the methods for sample preparation and the length of time required for testing. In spite of their limitations, these tests continue to comprise a major part of the surveillance programs of many countries, although they are being supplemented increasingly by more modern techniques.

Newer methods are based on instrumental techniques which are much more sensitive than the traditional methods. Because of this, the accuracy attainable with stability predictions based on them is greatly improved over that from the older tests. Much smaller changes can be detected in the aged propellant and accurately

related to the safe shelf life. Sample preparation techniques have also become more refined. This has resulted in increased confidence in the integrity of the samples.

Among the newer methods, the extent to which each has been developed and implemented for surveillance varies. Thus the relatively simple apparatus for TLC and HPTLC makes these methods readily adaptable for routine use. However they are no longer used for surveillance because there is greater facility for quantitative results with HPLC. This is currently the most favoured surveillance method and some countries have already implemented surveillance programs based on it. Several others are currently developing such a program.

Microcalorimetry is another instrumental technique which is very highly regarded. However, its development and implementation as a surveillance method is not yet as widespread as that of HPLC. Other instrumental methods have been adapted for surveillance but to a much smaller extent; these include GC, GPC, and viscosimetry. The remaining modern methods, such as chemiluminescence, DTA/TGA, MS, and DSC, have not yet been sufficiently developed for implementation in surveillance programs. However, some of these methods, particularly chemiluminescence, have given valuable information about propellant decomposition.

Thus there are two principal choices for a country wishing to revise its program of stability surveillance. Firstly, it can retain one or several traditional test methods, or adopt modified

versions of these. Secondly, it can adopt one or several of the modern test methods, which are believed to give a more accurate picture of the chemical evolution of the propellant.

The decision to maintain some traditional methods or to adopt newer methods is often based upon the availability of resources for the development and implementation of the modern techniques. But when the traditional tests are found to give incorrect or inconsistent stability predictions, then the need for change must be addressed. As a result of such situations, many countries have already updated their surveillance programs. Their willingness to share their expertise has provided the rest of us with valuable and time-saving information about the old and new methods. As well, it should greatly facilitate our decisions about our future surveillance programs.

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