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A New Stability Concept for Propellants

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Abstract. The chemical stability tests currently used for propellants suffer from some drawback. In this paper an attempt has been made to recast the existing system of stability testing in order to improve the reliability factor. A new stability concept has also been brought out based on the action of the stabilizer and its derivatives with the decomposed products of the nitric esters, the chief constituents of the propellants.

1. Introduction

Almost all conventional solid propellants[1-3] currently used in service contain nitrocellulose and nitroglycerine. Being nitric esters nitrocellulose and nitroglycerine are somewhat less stable and tend to decompose even at normal conditions of storage. The decomposition of propellant follows a series of complex reactions involving NO_2, NOand free radicals. The oxides of nitrogen evolved as primary decomposition products react with the residual moisture present in the propellants and form nitrous and nitric acids which catalyse and accelerate the decomposition process. To achieve satisfactory stability of propellants, it is customary to add stabilizer into propellant formulations. They react with the oxides of nitrogen and the acids so that these oxides/acids are removed from the system before they can catalyze the decomposition reaction.

Lack of adequate stability reduces safe life of propellants seriously leading to hazards in handling, storage and use. Stability tests, therefore, have unquestionable importance in quality assurance of propellants.

Though many stability tests are in current use, almost all of them suffer from some drawback or the other. At present, to have a completely reliable stability test which is a sufficiently rapid, easy, economical and factual in assessment, is a difficult problem. It is being pursued by researchers all over the world actively and it may take quite sometime before completely satisfactory stability test is developed and established. Propellant manufacture in the country is on ever increasing scale both in quantity and variety. It is, therefore, necessary to make some better working

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arrangements to assess stability of propellants, in general, especially of propellants with doubtful stability. In this paper an attempt has been made to reassess and recast the existing system of stability testing.

Further, as per the existing concept of stability a propellant is termed as unserviceable/unsafe in which the concentration of the stabilizer falls half to its original value on storage. This leads to rejection of large quantity of propellants. A new stability concept, more scientifically based on a number of experiments/trials, has been brought out for implementation in the propellant industry.

2. Experimental Results

The following propellants for the present study were taken.

(1) NC 688 (single base) containing NC 98.5%, Diphenylamine 1 % as stabilizer, and other additives.

(2) NC 1066 (single base) containing NC 91 %, Diphenylamine 1.2% as stabilizer, and other additives.

(3) T-28 (double base) containing NC 65-69 %, NG 24-26% Carbamite, 5.5-6.5% as stabilizer, and other additives.

(4) NQ 018 (triple base) containing NC 20-21 %, NG 20-21 %, Picrite 54-56%, Carbamite 3-4%, and other additives.

These were subjected to the commonly applied stability tests[2] and the results obtained have been shown in Table 1, 2 and 3.

Often direct comparison of the results of a propellant obtained from the various stability tests gives misleading inferences. To avoid such situation, certain 'norms' are required for various stability tests. In the present work, such norms have been tried based on the limits laid down in the various standards and the available literature to facilitate prescription of more factual standards for various propellants.

To conclude overall judgement on stability, based on the various stability tests, propellants were subjected to Climatic Hut Trial conditions (CHT, storage at 50°C for 1-2 years) and sometimes prolonged surveillance Test (heating sample at 80°C for 2-3 weeks and observing whether brown fume evolves). They provide important information as to whether the propellants are likely to decompose at abnormally high rate or otherwise under normal storage conditions. Life assessment on CHT concludes overall judgement formed in respect of stability of propellants based on variety of tests.

3. Observation and Discussion

The usual procedure in most of the stability tests is to subject a propellant sample to a raised temperature and obtain a quick indication of stability by determining the extent of decomposition. It is assumed that the decomposition of the propellant during the short period of stability tests is equivalent to the decomposition that would occur in several years of storage at ambient temperature.

Table 1. Results of stability tests on propellants

Propellant	Abel Heat test (minutes)	Methyl Violet test (minutes)	Berjman and Junk test (ml. of NO/5g)	Dutch test % weight loss during last 64 hours	Woolwich test at 80°C, percent stabilizer: Before test	After test	%fall in stabilizer
NC 688	15.5, 16 (at 80°C ≮30′)	40, 40 (at 134°C ≮40′)	9.5, 8.5 (at 132°C ≯9.5)	1.9, 2.3 (at 110°C ≯2%)	0.85	0.64	0.21
NC 1066	20, 20 (at 80°C ≮10′)	45, 45 (at 134°C ≮50′)	8.4, 9.0 (at 132°C ≯8.5)	2.0, 2.4 (at 110°C ≯1.5%)	1.08	0.90	0.18
T-28	8.5, 9.0 (at 71°C ≮10′)	40, 40 (at 120°C ≮40′)	2.8, 3.0 (at 105°C ≯5.8)	2.8, 2.7 (at 105°C ≯2%)	5.94	5.35	0.59
NQ 018	10, 10.5 (at 65°C ≮10′)	45, 45 (at 120°C ≮40′)	1.3, 1.3 (at 120°C ≯4)	2.6 (at 105°C ≯2%)	3.81	3.41	0.40

Figures shown in brackets indicate the acceptance limits for the propellants as per the current standards.

For determining the extent of decomposition some chemical or physical parameter which monitors decomposition is measured, such as :

(1) Measurement of consumption of stabilizer (e.g. Woolwich test)

(2) Measurement of heat of exothermic decomposition reaction (e.g. Silver Vessel test).

(3) Measurement of evolved gases :

(a) by indicators depending on the action of NO and NO_2 (e.g. Abel Heat test, Methyl Violet test),

(b) by direct observation of brown fumes.

(c) by quantitative estimation of decomposition products (e.g. B & J test).

(d) by determination of loss of weight (e.g. Dutch test and Small Vessel test).

(e) by gasometric method (e.g. Vacuum Stability test).

Production and acceptance testing of propellants require rapid assessment of stability which in turn demands use of higher temperature during stability testing. Reactions occurring during decomposition are complex, and detailed machanism for the effect of high temperature and other test conditions is largely unknown.

The possibility of occurrence of reactions not significant during decomposition at ambient storage temperature, renders high temperature stability tests somewhat

Table 2. Detection of derivatives of the stabilizer used

Propellant	Stabilizer used	Percentage of stabilizer (heating at 80°C for four weeks)		Presence of Derivatives of stabilizer used, after the test		
		Before the test	After the test	N-Nitroso DPA	Mononitro DPA	Dinitro DPA
Single base propellant NC 688 (India)	DPA	1.01	0.35	Present	Present	Absent
Single base propellant NC 1060 (India)	DPA	1.22	0.60	Present	Present	Absent
Single base powder for 7.62 mm (Bulgaria)	DPA	1.26	0.42	Present	Present	Absent
Cartg-QF 57 mm HEAT (Belgium)	DPA	0.93	0.29	Present	Present	Absent
NRKN for 7.62 mm (ICI)	DPA	1.13	0.48	Present	Present	Absent
Single base propellant for 7.62 mm (Belgium)	DPA	1.06	0.36	Present	Present	Absent

Presence of various derivatives of DPA was detected with the help of TLC and with spot tests.

Table 3. Stability status of the propellants

Stability Test	Propellants			
	NC 688	NC 1066	T-28	NQ 018
Abel Heat Test	Inferior	Superior	Adequate	Adequate
Methyl Violet Test	Adequate	Adequate	Adequate	Adequate
B & J Test	Adequate	Adequate	Superior	Superior
Dutch Test	Adequate	Inferior	Inferior	Inferior
Woolwich Test	Excellant	Excellant	Superior	Superior
Surveillance Test	Superior	Superior	Superior	Superior

unreliable. For more factual assessment of stability, tests employing low ageing temperature are preferable. However, low temperature tests take unduly long time and lead to hold-ups and delays, if applied to production/acceptance testing. For surveillance of propellants undergoing storage, long duration tests may be acceptable to some extent yet large magnitude of such work may find their routine application inconvenient.

Under the present study, observation on the results of various tests conducted on the propellants under Table 1, indicates in a general way the implications in respect of stability. Direct comparison of the results of different tests on a propellants sometimes gives misleading conclusions as the various stability tests give diverse results.

As in these test many variables which may have an important bearing on the test results, are fixed differently, their results are not on a common ground. To compare them directly is not a sound proposition. If it is possible to provide some common basis, their comparison can produce some fruitful results.

In order to provide an approach for better correlation of the results of different tests certain norms corresponding to 'adequate', 'inferior' and 'superior' stability have been laid down for different stability tests and propellants studied as shown in Table 3.

Comparing results of different tests with the proposed norms stabilities have been graded accordingly as adequate, superior and inferior. The stability so graded, for each of the propellants, by different stability tests has been compiled and given in Table 3. Perusing the results of this table vertically i.e. by considering the graded stabilies for each propellant by different stability tests an overall judgement can be formed, regarding the stability of each propellant individually. Such judgement for all the propellants under present study, works out that they all possess moderately superior stability i.e. good stability.

To conclude this overall judgement of possession of 'good stability' the propellants were subjected to CHT conditions (at 50°C for 1 year in case of T-28 and for 2 years in case of other propellants). CHT conditions represent ageing at sufficiently low temperature compared to most of the stability tests. Based on kinetic factor of 1.8 per 10°F, one and two years storage in CHT corresponds to about 5.5 and 11 years of ambient storage.

If any of the propellant under present study possessed inadequate stability it would have been reflected in rapid decomposition during CHT storage, by excessive fall in the results whereas they do not show such fall. The results, therefore, support the overall judgement of possession of 'good stability' for all the propellants under the study.

Horizontal perusal of Table 3 i.e. assessment of stability of different propellants by a single stability test shows performance of the stability test. If assessment of stability on different propellants made by an individual stability test is close to the overall judgement on stability of the particular propellant made by several stability tests the performance of the tests is considered to be more reliable and its assessment of stability is likely to be more factual. Consistency of the four assessments (on the four propellants studied) among themselves by a particular test also offers clue to the consistency in working/performance of the test.

By judging in this way, B & J test, Methyl Violet test, Small Vessel test and Surveillance test appear more reliable. Abel Heat test and Woolwich test appear to have moderate reliability, whereas Dutch test shows dubious reliability. Though all the four assessment by Dutch test deviate from the 'consensus' they do so almost consistently. This may be due to some stable feature connected with the set up/ apparatus of the test or some faulty operation or assumption and calls for deeper investigation into the working of the test.

As per present practice, normally the period in which the concentration of the stabilizer falls half of its original value is taken as 'Safe life'. Here, based on the experimental findings/evidences[1-4] it is suggested that as long as nitroso derivatives of stabilizers are present in the sample, the propellant should be considered completely safe and having good stability, even if the stabilizer as such might have been consumed completely. Even in cases where no nitroso compound is found, only mononitro derivative is present but if no dinitro derivative of the stabilizer is found present, the propellant should be regarded equally serviceable as the stabilizing power of a stabilizer, its nitroso derivative and its mono-nitro derivative is almost same. This has also been seen experimentally (Table 2). It would, therefore, be not worthwhile to reject the propellant on finding the fall of the concentration of stabilizer to half of its original value but to view them with new concept as suggested above. It is, therefore, recommended that the propellants should be tested for nitroso, mononitro and dinitro derivatives of the stabilizers used and not for the fall in percentage of stabilizer as such.

4. Conclusion

Based on the results obtained under the present study following conclusions are drawn :

(i) Satisfactory correlation amongst the test results of common stability tests is not easily found. However, some correlation can be achieved by their comparison with some 'norms' for different levels of stability.

(ii) Too much reliance on Abel Heat test is not desirable. B & J test and Methyl Violet test which have good reliability can be adopted for all the propellants.

(iii) As far as possible minimum three stabiltity tests should be specified in the governing standards to derive the "Stability Status" of the propellant more reliably.

(iv) A new stability concept has been brought out as per which a propellant can still be considered serviceable if nitroso and mono-nitro derivatives of the original stabilizer used are found to be present in the propellant even if the presence of original stabilizer as such may be negligible but in no case any dinitro derivative of the stabilizer should be present.

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