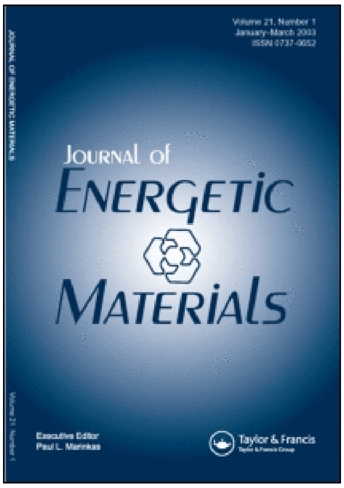

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Peshave, J. R. and Singh, Haridwar(2002) 'Determination of chemical life of combustible cartridge cases', Journal of Energetic Materials, 20: 4, 345 — 356
To link to this Article: DOI: 10.1080/07370650208244828
URL: http://dx.doi.org/10.1080/07370650208244828

DETERMINATION OF CHEMICAL LIFE OF COMBUSTIBLE CARTRIDGE CASES

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ABSTRACT.

Determination of the stability and prediction of the chemical life of Combustible Cartridge Cases (CCCs) which are extensively used in the high calibre tank gun ammunition is one of the major requirement for manufacturer. The results obtained by carrying out accelerated aging of CCC samples at elevated temperatures are discussed in this paper. The plot of residual stabilizer content (%) versus time (days) has been used in the Woolwich formula and Berthelot's equation to extrapolate the life at normal storage temperature, (30°C). Also chemical life was determined by subjecting CCC sample to standard Woolwich stability test.

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Journal of Energetic Materials Vol. 20, 345-356 (2002)
Published in 2002 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

Combustible Cartridge Case (CCC) is an important part of a Semi Combustible Cartridge Case (SCCC) ammunition, which is being used now a days in Tank Guns and self propelled howitzers all over the globe. The recent trend in the world is to achieve defeat of the target at longer range, which is possible by using higher calibre guns mounted on tanks achieving higher chamber pressure, resulting into higher muzzle velocity. Since brass starts yielding at higher chamber pressure (above 500 MPa), the only alternative left is to replace conventional brass cartridge cases by Combustible Cartridge Cases. In fact CCC reduces logistic problem of removal of cartridge case from tank and cost wise CCC technology and products are very attractive. CCCs also act as propellant as they burn alongwith the propellant which contains in them and thus produce an additional energy. Hence CCCs were subjected to life assessment as per propellant assessment.

Since most of the literature on CCC compositions and CCC technology is either classified or patented, in India an indigenous technology based on felting technique was developed. CCCs are made[1,2] from nitrocellulose (NC), nitroguanidine (Ngu) and cellulosic fibres, keeping in view their compatibility with the propellant used in the SCCC ammunition. Diphenylamine (DPA) is used as a stabilizer in the CCC formulation in order to enhance their chemical life.

Nominal composition of CCC

	Ingredient	Percentage
*	Nitrocellulose (12.6 % Nitrogen content)	~ 60
*	Cellulose	~ 15
•	Nitroguanidine (picrite)	~ 20
*	Diphenylamine	~ 1
•	Dibutyl phthalate	~ 4
*	Copper naphthenate	~ In traces

CCCs need to be stored before their assembly in the ammunition. Also, the ammunition assembled with CCC may have to be stored in the magazine for a longer period prior to their dynamic trials. Hence, life evaluation of CCC is one of the major requirement and hence a systematic study on CCC was carried out by aging the samples at accelerated temperatures to predict the chemical half life.

STABILITY

Prolonged storage might result in deterioration of energetic ingredients in CCCs. Moreover, ingredients may interact with each other or get affected by atmospheric conditions to produce irreversible changes that can seriously affect their stability, and the ballistic as well as mechanical properties. Chemical changes may occur due to thermal, oxidative or hydrolytic reactions resulting in softening, hardening, swelling, discoloration of CCCs with the evolution of gases.

Brook et al[3] have reported that propellant based on NC decomposes significantly at normal storage temperatures. The products of decomposition are acids and oxides of nitrogen, which catalyze the decomposition process. The reaction is exothermic, which causes self heating of the propellant. This under certain circumstances, may lead to auto-ignition. To prevent these autocatalytic reactions from occurring, and to reduce the rate of decomposition of the propellant during the storage, various stabilizers are added to propellant formulations. The function of a stabilizer is to react rapidly with the nitrogen oxides and acids formed due to decomposition so that they are removed from the system before they can catalyze further decomposition. Thus, the propellant life can be increased.

The decomposition of propellant passes through successive phases such as formation of traces of nitrous acid (HNO_2). Gases such as CO, CO_2, N_2, N_2O, NO, NO_2 etc. are gradually evolved[4,5]. However, these changes in the composition of the propellant during storage do produce a slow ballistic change generally in the downward direction i.e. lowering of Muzzle Velocity and Pressure. The aging reactions are accelerated as the temperature of the storage increases[6].

If NC is stabilized[3], it can be safely stored for many years. With this view, some valid tests have been devised to check whether NC in the composition has been adequately stabilized. In majority of the stability tests, the propellant containing NC is artificially aged by heating. It is an established fact that the decomposition of the propellant that occur during the short period of the stability test is equivalent to the decomposition that would occur in several years of storage at ambient temperatures.

According to another study[7] measurement of stabilizer content showed that the propellant was still in a safe condition even though there was virtually no stabilizer (DPA) present. The nitrated derivatives of DPA continued to act as effective stabilizers. Their presence makes prediction of future safe life of such propellants difficult since DPA was commonly used as the sole basis for the determination of safe life of propellants. The propellant stability was assessed on the basis of the amount of stabilizer present. It has been found that a single base propellant with very low DPA content can continue in a safe condition for several years.

Predictive methods for judging safe life are generally based on measurement of stabilizer content after accelerated aging. Such methods may give reliable estimates of stabilizer content and the time at which this will reach a specified low level, but predictions of ultimate safe life cannot be made. Hence, in the recent years number of researchers in many countries have used modern instrumental techniques to measure the low residual stabilizer and its nitrated derivatives to predict the correct life of the propellant.

Role of stabilizer

As NC is a major energetic ingredient of CCC, the chemical decomposition processes occurring in single base propellants with NC may also occur in CCC. Since NC may decompose significantly even at ambient storage and the decomposition reactions are exothermic, the possible self heating of NC leading to self ignition may also occur in case of CCC. Hence DPA is used as a stabilizer in the CCC formulation.

DPA forms salt with acids. DPA is a non-explosive compound, possessing the property of absorbing and reacting with nitrogen oxides. DPA is widely used as a stabilizer (content ~ 1%) in the single based propellants[8] as gases like nitrogen and nitrogen oxides are generated during the storage of propellant. Muraour[9] stated that the role of DPA is to maintain the rate of decomposition within certain limits and to prevent its acceleration. However, owing to its basic character, DPA must not be used in large quantity. Otherwise, it attacks NC even at the temperatures as low as 40°C and these reactions are accelerated at high temperatures.

AGING METHODS

Accelerated aging methods

In this method the propellant samples are stored at elevated temperature and the chemical changes are monitored. An empirical criterion is set to distinguish unstable propellants from stable ones. Though this method offers quicker means for aging studies, the main drawback of this technique is that the measured values may not permit any direct correlation with the behavior of the propellants stored at normal temperature.

Methods of the life estimation of the propellants are as follows :

i) Time required for 50% depletion of the original stabilizer content is taken as a measure of chemical life of propellant. Samples are subjected for standard Woolwich test[4] (80°C) to determine the chemical life.

ii) In another scheme the rates of stabilizer depletion at high temperatures are measured and extrapolated to lower temperatures. The time required for reaching the stabilizer concentration to half of its original is then determined for normal storage temperatures and chemical life is determined by following Woolwich formula[10] and Bethelot's equation[11].

EXPERIMENTAL

Stabilizer depletion of CCC

Combustible Cartridge Cases from accepted lot were selected randomly and cut into strips of size 100 x 25 mm. These strips were kept in the specially designed oven to study the stabilizer depletion. Samples were withdrawn at fixed intervals of days after accelerated aging at 70°C, 80°C and 100°C and estimated for stabilizer content. The stabilizer was determined by subjecting the ether extracts of the samples to HPLC.

The chemical life of CCC was assessed by plotting the percentage residual stabilizer (DPA) content (%) versus Aging Time (Days) by using Berthelot's equation.

Woolwich test at 80°C for 3 weeks

5 g of CCC sample.was subjected to standard Woolwich test[4] to determine the chemical half life.

RESULTS AND DISCUSSION

Chemical Life

Results for DPA depletion are given in Table - 1 for CCC samples aged at 70°C, 80°C and 100°C. Considering time for depletion of stabilizer content by 0.25 taking 1.05 % as reference for samples aged at 70°C, 80°C (Fig. 1) and 100°C (Fig. 2), the half life values were obtained by applying Woolwich formula. The results obtained indicate half life of 71.8 days, 24.6 days and 1.49 days respectively.

Thus, the half life estimates obtained by applying Woolwich formula gave a factor of 2.92, corresponding to increase in rate of CCC aging with increase in temperature by 10°C, which was worked out by dividing the half life at 70°C with that at 80°C. However, this factor was not found suitable for back calculation of the half life at 70°C and 80°C using half life at 100°C (1.49 days) in the Berthelot's equation. The values were observed much less. This may be due to consumption of more amount of DPA at 100°C which might have resulted in less half life. Because at 100°C heating, initial nitrogen oxides in NC of CCC formulation and traces of moisture will form HNO_3 which will further catalyze the rate of decomposition reaction and in order to arrest this decomposition, more amount of stabilizer will be consumed and hence less half life at 100°C. However at 30°C, the rate of decomposition of NC from CCC will be much lower as compared to that at 100°C and hence less amount of DPA will get consumed to arrest the possible decomposition of NC. Hence, Berthelot's equation can be applied for calculation of half life at 30°C. By using factor as given above (2.92) and the half life obtained at 70°C, half life of the CCC at 30°C works out to be 14.3 years.

Chemical half life by Woolwich test

The initial DPA content was found to be 1.02 % in the CCC sample which was subjected to Standard Woolwich test. After completion of the test, the value obtained was 0.695 % . Using these values in the standard Woolwich formula, the chemical half life (L) of CCC was calculated to be 19.0 years at 30°C.

Thus, the half life obtained from standard Woolwich test is in agreement with the half life estimated using Berthelot's equation.

CONCLUSION

The results of present study suggest that the chemical half life of CCC is minimum 14 years. CCCs are chemically stable and safe for storage and handling at 30°C for minimum 14 years.

ACKNOWLEDGEMENT

The authors are thankful to Shri B.Y. Deshpande and Miss S.H. Kulkarni for the necessary help extended by them during testing the samples after the accelerated aging.

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Table 1 : Results of DPA depletion on aging of CCC

Conditioning temperature (°C)	Interval (Days)	Residual DPA content (%)	Half life as per Woolwich formula * (Days)	Half life at 30°C computed from 70°C data (factor 2.92) (Years)
70	0 14 28 35 42 49	1.05 0.83 0.80 0.78 0.76 0.67	71.8	14.3
80	0 6 9 12 15	1.05 0.90 0.85 0.80 0.71	24.6	
100	0 0.5 (12 hrs.) 0.75(18 hrs.) 1 (24 hrs.)	1.05 0.81 0.76 0.67	1.49	

* Time for depletion in stabilizer content by 0.25 has been used in Woolwich formula

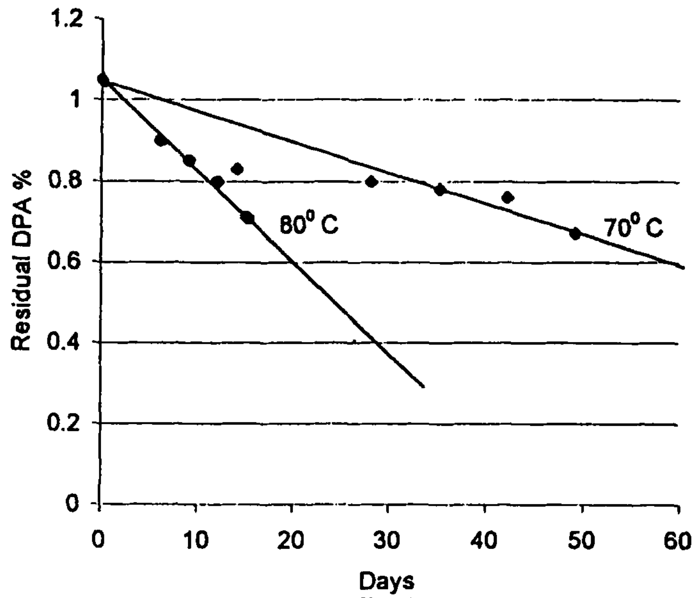

Fig. 1

DPA depletion due to aging at 70^{0}C and 80^{0}C

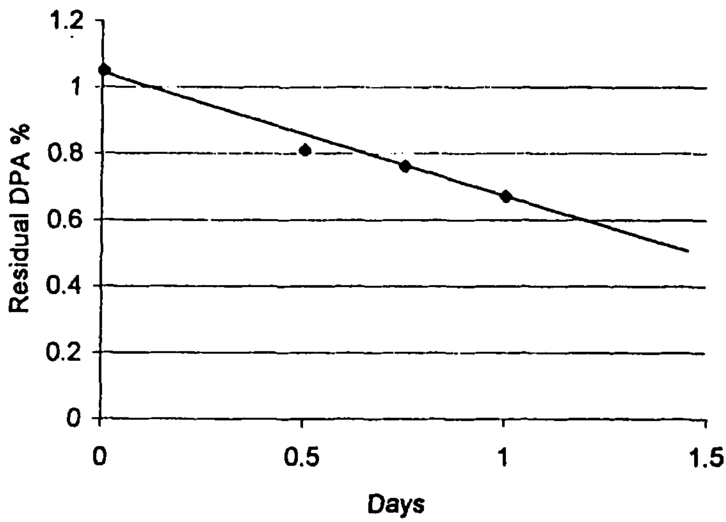

Fig. 2

DPA depletion due to aging at 100^{0}C