SHORT COMMUNICATION

Observation of Change in Colour of Combustible Cartridge Cases on Ageing—A Qualitative Tool

J.R. Peshave and Haridwar Singh

High Energy Materials Research Laboratory, Pune-411 021

ABSTRACT

The stability of combustible cartridge cases (CCCs) which are extensively used in the high calibre tank gun ammunition is one of the major requirements for their safe handling and storage. The results of stability tests by heating of CCC samples at elevated temperatures and observations for change in colour of the CCC samples have been discussed. It has been observed that there are drastic changes in the colour of the CCC samples. The original pale yellow colour of the uncoated internal surface was changed to dark green. Similarly, original yellowish-brown colour of external surface coated with shellac varnish was changed to dark greenish-brown.

Keywords: Combustible cartridge case, tank gun ammunition, ageing, handling and storage

1. INTRODUCTION

Extensive use of combustible cartridge cases (CCCs) in the high calibre tank gun ammunition all-over the world is well known. The CCCs replace conventional brass cartridge cases as these reduce logistic problems of removal of spent cartridge cases from a tank, as only metallic base stub gets ejected after the firing. Moreover, it is suitable for autoloading as well as firing above 450 MPa chamber pressure.

In India, the CCCs are made \(^1\) from nitrocellulose (NC), nitroguanidine (NGu) and cellulosic fibres by felting technique, keeping in view their compatibility with the propellant used in the semi-combustible cartridge case (SCCC) ammunition. Diphenylamine (DPA) is used as stabiliser, to enhance the chemical life of the CCC. Dibutyl phthalate (DBP) is added as plasticiser for easy processing and copper naphthenate is used as an antifungal agent.

The composition of the CCC is comparable with single-base propellant as it contains 60 per cent nitrocellulose, the main energetic ingredient and does not contain any nitric ester plasticiser. Since NC is known to decompose during storage, the CCCs are likely to degrade on storage, which may lead to their reduced ballistic performance.

2. IMPORTANCE OF STABILITY TESTS

All conventional propellants containing NC with or without nitroglycerine (NG) are metastable explosives in general and are liable to decompose with the consequent formation of free acids. The decomposition is accelerated, particularly by the oxides of nitrogen, and the acids are formed during decomposition. This rate of decomposition depends on the temperature and the humidity during storage and also the extent of storage period.
The CCCs need to be stored before their assembly in the ammunition. Also, the ammunition assembled with the CCCs may have to be stored in the magazine for longer durations prior to their intended end use. Since the CCC contains NC to a large extent, it is expected that prolonged storage of the CCCs may result in their deterioration and these undergo colour change due to decomposition of the NC. The stability tests applicable to NC can be used for the CCCs to evaluate their ageing characteristics.

3. EXPERIMENTAL PROCEDURE

The CCCs from a single batch were selected randomly and cut into strips of 100 mm x 25 mm. These strips were kept in the specially designed oven at elevated temperatures. Samples were withdrawn at fixed intervals (of days) after heating at 70 °C, 80 °C, and 100 °C, and visual observations were made for any change in colour. Samples were subjected to methyl violet (MV) test at 134.5 °C and Abel heat test at 82.2 °C. Residual stabiliser content of each sample was determined by subjecting the ether extracts of the sample to HPLC (Perkin Elmer Series 410 LC Pump, LC-90 Detector and Column -C-18, HPLC grade DPA was used as standard).

4. RESULTS & DISCUSSION

4.1 Visual Observations—Colour Change

The results of the visual observations for change in colour of the CCC samples due to ageing at 70 °C, 80 °C, and 100 °C have been given in Table 1.

On aging at 70 °C, the initial pale yellow colour of internal uncoated surface of the CCC was changed to greenish-yellow after 14 days and green after 35 days of ageing. After 49 days, the green colour changed to dark green. At 80 °C, the pale yellow colour changed to greenish-yellow after six days.

<table>
<thead>
<tr>
<th>Storage temperature (°C)</th>
<th>Time interval (Days)</th>
<th>Visual observation for colour change (internal uncoated surface)</th>
<th>MV test time at 134.5 °C (min)</th>
<th>Abel heat test time at 82.2 °C (min)</th>
<th>Residual DPA content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0</td>
<td>Pale yellow</td>
<td>45</td>
<td>15.0</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Greenish-yellow</td>
<td>30</td>
<td>10.0</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>Greenish-yellow</td>
<td>25</td>
<td>6.0</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>Green</td>
<td>23</td>
<td>5.5</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>Green</td>
<td>23</td>
<td>4.5</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>Dark green</td>
<td>22</td>
<td>4.5</td>
<td>0.67</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>Pale yellow</td>
<td>45</td>
<td>15.0</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Greenish-yellow</td>
<td>37</td>
<td>6.5</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Green</td>
<td>33</td>
<td>6.0</td>
<td>0.85</td>
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<tr>
<td></td>
<td>12</td>
<td>Green</td>
<td>26</td>
<td>5.0</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>Dark green</td>
<td>25</td>
<td>4.0</td>
<td>0.71</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>Pale yellow</td>
<td>45</td>
<td>15.0</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>0.50 (12 h)</td>
<td>Greenish-yellow</td>
<td>30</td>
<td>5.5</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>0.75 (18 h)</td>
<td>Green</td>
<td>25</td>
<td>4.5</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>1.00 (24 h)</td>
<td>Dark green</td>
<td>20</td>
<td>4.0</td>
<td>0.67</td>
</tr>
</tbody>
</table>
and turned green after nine days. After 15 days, the green colour changed to dark green. However, for samples aged at 100 °C for 12 h, the colour was greenish-yellow which subsequently changed to dark green after 24 h.

Initial yellowish-brown colour of external surface coated with shellac varnish turned to dark greenish-brown after 49 days, 15 days and 24 h of ageing at 70 °C, 80 °C, and 100 °C, respectively.

These results indicate that as the ageing temperature is increased, the original pale yellow colour changes to greenish-yellow, green, and subsequently to dark green for internal uncoated surface and dark greenish-brown for external coated surface. The change in colour to dark green and dark greenish-brown of both the internal uncoated and the external coated surfaces at higher temperatures suggest the gradual deterioration in thermal stability and possible consumption of more stabiliser to arrest the decomposition reactions of NC on ageing at higher temperatures.

As a part of this study, the CCC samples of different compositions were heated (i) with DPA and without copper napthenate, (ii) without DPA and with copper napthenate, (iii) without DPA and without copper napthenate, and (iv) reference sample, i.e., with DPA and copper napthenate at 100 °C for 8 h. Samples (i) and (iv) turned green, whereas samples (ii) and (iii) showed yellowish colouration, which indicates that reaction of DPA with NC on prolonged heating gives the green colouration which is more predominant at higher temperatures.

4.2 Methyl Violet & Abel Heat Tests

The results of the methyl violet and Abel heat tests are given in Table 1. These results suggest that as the ageing temperature and the period of ageing are increased, the time required to change the colour of the methyl violet paper gets significantly reduced, as expected. However, no brown fumes or explosion was observed, when the CCC samples were heated for 5 h at 134.5 °C.

In the case of Abel heat test, it was observed that at all the ageing temperatures, there was a reduction in the time of appearance of yellowish-brown line at the junction of wet and dry areas of the starch-potassium iodide paper. These results follow the normal expected pattern.

4.3 Residual Stabiliser Content

The results for residual stabiliser content are given in Table 1. Monitoring of DPA depletion by HPLC at 70 °C, 80 °C, and 100 °C at regular intervals (of days) showed gradual reduction in DPA content. This is in agreement with the colour change of the CCC samples on ageing and reduction in the test time of MV test as well as Abel heat test that certain amount of DPA has been consumed to arrest the possible decomposition reactions.

5. CONCLUSION

Results indicate that a drastic change in the colour was observed in the CCC samples aged at higher temperatures (70 °C–100 °C), which shows that more quantity of stabiliser gets consumed during accelerated ageing to arrest the possible decomposition of the NC from the CCCs. This observation was further confirmed by carrying out MV and Abel heat tests. The gradual reduction in the test time is in agreement with the visual observations of colour changes. These results reveal that more amount of stabiliser gets consumed to retard decomposition of the NC at elevated temperatures.

This study indicates that mere observance of colour change in the CCCs on storage for longer durations at ambient conditions, either in the form of the CCC sets or ammunition, may be an effective qualitative tool to take necessary disposal action on the spot, considering the safety aspects.

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REFERENCES


Contributors

Mr JR Peshave, Technical Officer C, joined DRDO at the High Energy Materials Research Laboratory, (HEMRL), Pune, in 1977. At HEMRL, he is engaged in the development of combustible cartridge case components for various artillery gun and tank gun ammunition. He did his MSc (PPPR) Chemistry from the University of Pune in 1999. He has been awarded with the DRDO Technology Award (1995) for the design and development of combustible cartridge cases for 120 mm FSAPDS and I-IESH SCCC ammunition and the NRDC Technology Innovation Award (1999) instituted by the Ministry of Science and Technology for the development of combustible cartridge cases for tank gun ammunition.

Dr Haridwar Singh is the outstanding Scientist and the Director of the HEMRL, Pune. Dr Singh has been honoured with the Agni Award (1998) for the excellence in self-reliance, the Astronautical Society of India Award (1994) for his significant contributions in the field of rocket and allied technologies, the DRDO Scientist of the Year Award (1983 and 1993), and the DRDO Cash Award. He is also the President of the High Energy Materials Society of India and a member of the Editorial Executive Committee of the Defence Science Journal and an honorary member of the Russian Academy of Aeronautics. He has 140 publications and 5 patents to his credit. He is a recognised postgraduate guide and a senate member of the University of Pune.