

## Polyvinyl Acetate Resin as a Binder Effecting Mechanical and Combustion Properties of Combustible Cartridge Case Formulations

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### ABSTRACT

Several combustible cartridge case (CCC) formulations containing nitrocellulose (NC) as an energetic ingredient with diphenylamine (DPA) as stabiliser, cellulose fiber as reinforcing material and polyvinyl acetate (PVAc) as a binder are processed to form combustible discs. A formulation containing nitrocellulose (83 parts), cellulose (17 parts), PVAc (20 parts) and diphenylamine (1 part) by weight was observed with the improvement of mechanical properties without any adverse effect on combustion characteristics, safety parameters and compatibility with triple base multi-tubular propellant. Dynamic firing performance was also satisfactory.

**Keywords:** Combustible cartridge case, binder, polyvinyl acetate, propellant case, tank ammunition, felting technique, resins, propellant formulations, PVAc resin

### 1. INTRODUCTION

Now-a-days, brass cartridge cases are being replaced by combustible cartridge cases (CCCs) in artillery and tank gun ammunition world wide because of their usefulness at high chamber pressure and for high firing rates<sup>1</sup>. The work done by many researchers on the formulation of CCC has been reported by Kurulkar<sup>2</sup>. High Energy Materials Research Laboratory (HEMRL), Pune, has developed<sup>3</sup> a formulation containing nitro-cellulose (NC), nitroguanidine (NGu), and cellulosic fibres and established manufacture of CCCs by the felting technique. The technology involves formation of matrix of cellulose and NC fibres with NGu as a filler. Mechanical strength of the combustible components is achieved by gelatinisation followed by compaction under high pressure. However, CCCs manufactured by this process do not possess the desirable mechanical strength.

Hence, a systematic study has been carried out to enhance the mechanical properties of CCCs without affecting the ballistic performance, by the incorporation of resin as a binder. The study reveals the use of polyurethane<sup>4</sup>, vinyl<sup>5</sup>, acrylic<sup>6</sup>, and styrene-butadiene<sup>7</sup>-type resins in the manufacture of CCCs. Various methods have been reported<sup>8-15</sup> such as felt-moulding, winding or impregnation of resin in the felted combustible components to achieve the desired mechanical properties. However, the information reported in the literature is either classified or patented. In the present work, a systematic study has been carried out on different formulations of CCCs using commercial PVAc resin available in the dispersion form.

#### 1.1 Criteria for Selection of Ingredients

Criteria for selection of cellulose, NC, and diphenylamine (DPA) are well known<sup>2</sup>. However, PVAc binder has been selected due to its well-known adhesion property with cellulosic materials

due to its polar acetyl groups<sup>16</sup>. The acetate of the binder can form physical bond with cellulosic material<sup>16</sup>. Being insoluble in water, its retention in NC-cellulose matrix during felting of the preforms in aqueous medium and the best results are obtained with smaller resin particles forming a sheath around each individual fibre. Also, because of the presence of atactic acetyl groups, PVAc is flexible and soft with  $T_g$  of 28 °C and a lower degree of branching present in PVAc contributes to some stiffness at room temperature. Considering all these aspects, PVAc resin having molecular weight of about 5 lakh, has been used in the present study.

The formulations under study contained NC (12.6 % N) as a main energetic ingredient with cellulosic fibres as reinforcing material and polyvinyl acetate as a binder in the dispersion form and DPA as a stabiliser. The CCC discs are prepared using beater additive process followed by hot compaction.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Materials

Nitrocellulose (12.6 % N) obtained from the ordnance factory, PVAc, under the trade name Pidivyl-AS resin, obtained from the Pidilite Industries, Mumbai, cellulose and DPA of desired purity were obtained from trade sources and their purity was checked before use. Table 1 shows the analysis results of these ingredients.

### 2.2 Equipment

The various equipment used for processing include beater, felting machine, water-squeezing unit, steam-heated dryer and hot-compacting machine, etc. Closed vessel<sup>17</sup>, Hounsfield tensometer, DTA, vacuum stability apparatus and methyl violet test apparatus were used for ballistic evaluation, improvement of mechanical properties, determination of decomposition

**Table 1. Analysis results of raw materials as ingredients of the formulations**

Material	Results	Specified limits	Source of supply
<b>Cellulose</b>			
a) Organic matter soluble in ether, alcohol (%)	0.20	0.4 max	M/s Sri Haripalayam Oilseeds Processing Co., Theni, Tamil Nadu
b) Ash content (%)			
c) Degree of freeness (ml)	0.25	1.0 max	
	195	180 min 200 max	
d) $\alpha$ -cellulose content (%)	97.8	> 95	
<b>Nitrocellulose (NC)</b>			
a) Nitrogen content (%)	12.52	12.6±0.1	O. F. Itarsi
b) Mineral matter (%)	0.28	0.8 max	
c) Alkalinity (%) (calculated as $CaCO_3$ )	0.38	0.4 max	
d) Organic matter insoluble in acetone (%)	Traces	0.5 max	
e) Heat test at 80 °C (min)	16	10 min.	
<b>Polyvinyl Acetate resin</b>			
a) Solid content (%)	49.0	48 min.	M/s Pidilite Industries, Mumbai
b) Viscosity @ 30 °C (Brookfield, RVT, Spindle 7, 20 rpm) (poise)	762	500 – 1100	
c) pH	5.1	6	
d) Mol. wt. (wt. avg.) (Lakhs)	4.6	4.5±0.5	
e) Particle size ( $\mu$ m)	2.62	1 – 3	
f) Ash content (%)	0.33	< 0.5	
<b>Diphenyl amine (DPA)</b>			
a) Moisture (over caustic potash in a vacuum desiccator) (%)	0.032	0.5 max	Local trade
b) Reaction			
i) Alkalinity	Nil	Nil	
ii) Acidity as $H_2SO_4$ (%)	Nil	0.005 max	
c) Organic matter insoluble in ether, alcohol (%)	Nil	0.02 max	
d) Mineral matter (%)	0.0048	0.05 max	
e) Setting point (°C)	53	51.5 min 53.0 max	

temperature, vacuum and thermal stability of the CCC, respectively.

### 2.3 Composition/Formulation

To establish the process parameters of hot compaction, viz., temperature of mould and compaction pressure, basic composition with NC: 80 parts, cellulose: 20 parts, PVAc: 20 parts, and DPA: 1 part by weight has been used (Table 2). Furthermore, eight compositions varying in PVAc content (Table 3) and NC: cellulose ratio (Table 4)

**Table 2. Effect of process parameters temperature and pressure on physico-mechanical properties of CCC discs (NC: 80, cellulose: 20, PVAc: 20, DPA: 1)**

Process parameters		Density (g/cm <sup>3</sup> )	TS (MPa)	E (%)
Pressure (MPa)	Temp. (°C)			
3.9	105	0.84	14.5	4–5
4.9	105	0.97	16.6	4–5
5.9	105	0.98	17.7	4–6
6.9	105	1.03	22.2	4–6
7.9	105	1.03	17.9	4–5
6.9	60	0.73	7.1	6–7
6.9	70	0.73	7.6	6–7
6.9	80	0.81	11.9	5–7
6.9	90	0.87	13.2	5–7
6.9	105	0.97	20.2	6–8
6.9	115	---Sample deformed---		

**Table 3. Effect of PVAc content on physico-mechanical properties of CCC discs (NC: 80, cellulose: 20, DPA: 1) compacted at 105 °C and at 70 kg/cm<sup>2</sup>**

PVAc by parts	Density (g/cc)	TS (MPa)	E (%)
15	0.86	16.0	6–7
20	1.05	24.6	8–10
25	1.05	26.1	8–10
30	1.06	25.5	9–11

**Table 4. Effect of NC: cellulose ratio on physico-mechanical properties and combustion characteristics of CCC containing PVAc (20 parts) and DPA (1 part)**

Ratio of NC : cellulose (parts by weight)	Physico-mechanical properties			Combustion characteristics	
	Density (g/cc)	TS (MPa)	E (%)	Rise time (ms)	dP/dt (MPa/ms)
89 : 11	0.92	19.4	6–7	3–4	58
86 : 14	0.98	22.0	7–8	4–5	53
83 : 17	1.05	23.1	6–7	8–10	38
80 : 20	1.11	24.2	6–8	9–12	25

were prepared for making the CCC discs for optimisation of resin content and final composition, respectively.

### 2.4 Processing

#### 2.4.1 Slurry Preparation

Slurry preparation has been carried out by pulping dry cellulosic fibres to the desired freeness (50-70 CF number) in aqueous medium in a beater. The requisite quantity of NC and alcoholic solution of DPA were added to the slurry. Required quantity of diluted resin was then added under constant stirring. The mixture so obtained was then diluted with water to get 1 per cent solid and used for felting of the CCC discs.

#### 2.4.2 Felting Operation

The slurry was then taken in a disc-making machine to form the discs under vacuum. The thickness and the weight of the discs were controlled by feeding measured quantity of slurry. Water from felted discs was then removed by pressing between the two perforated aluminium plates at 0.3 MPa and the discs were dried in a steam-heated oven at 60±5 °C.

#### 2.4.3 Hot Compaction

Strength was imparted to the dry-felted CCC disc by pressing it in preheated metal moulds for a specified duration using a hydraulic press at 6.9 MPa. The pressed discs were allowed to cool at ambient temperature. Samples thus prepared from these discs were subjected to different tests. Table 2 shows the effect of pressure as well as temperature on the strength of the CCC.

For dynamic evaluation, a few CCC components in the final dimensions suitable to tank firing were prepared (Fig.1), using the same procedure of slurry making, felting, and hot compacting as described earlier. Ammunition preparation was carried out and these were subjected to dynamic firings and evaluated for combustion and ballistic performances.

## 2.5 Evaluation

### 2.5.1 Mechanical Properties

#### 2.5.1.1 Density

Density of resin-based CCC discs was determined by Archimedes principle using *n*-heptane. The CCC pieces of size (10 mm × 10 mm) have been used for this purpose.

#### 2.5.1.2 Tensile Strength

Test specimens were prepared by cutting strips (100 mm × 25 mm × 2.5 mm). Five specimens are tested with Hounsfield machine for tensile strength and percentage elongation (Model: Hounsfield-H25K5, Make: UK). For recording the events, the speed of crosshead was maintained at 50 mm/min. The results of mechanical properties are presented in Tables 2 and 3.

### 2.5.2 Closed Vessel Firing

Sample pieces (100 mm × 25 mm) were cut from the CCC discs. These samples having a charge

mass (140 g) were used for the closed vessel firing. (5 g) Gun powder (G-12) was distributed loosely on the CCC charge for ignition of CCC strips (140 g).

The output of CV data acquisition system was fed to the computer and the ballistic parameters, viz.,  $dP/dt$  and the rise time were computed. The results are shown in Table 4.

### 2.5.3 Thermal Stability

Combustible cartridge case samples were evaluated by methyl violet (MV) test at 134.5 °C. Results obtained are presented in Table 5. Also, the decomposition temperature was determined from DTA curves (Fig. 2).

### 2.5.4 Ash Content

Ash content was determined by muffling the sample at 800 °C.

### 2.5.5 Sensitivity

The impact and friction sensitivity of the CCC samples were determined by the standard methods and the data is presented in Table 5.

### 2.5.6 Flame Temperature

Flame temperature was measured using R-type thermocouple (platinum-platinum.rhodium) on



Figure 1. Photograph of resin-based CCC sets before dynamic firing.



Figure 2. DTA curve of optimised resin CCC formulation.

digital temperature indicator. The results are presented in Table 5.

### 2.5.7 Compatibility

Compatibility of the CCC samples was determined by the vacuum stability test at 100 °C and the data is reported in Table 6.

### 2.5.8 Analysis

Analysis of finally selected formulation of the CCC discs was carried out by gravimetric and HPLC methods, and the results are given in Table 7. However, cellulose and PVAc are reported together as there was difficulty in complete isolation of PVAc from the CCC matrix.

**Table 5. Stability and sensitivity data on PVAc-based CCC and conventional picrite-based CCC**

Test	Picrite CCC	Resin-based CCC
M.V. test at 134.5°C, time (min)	45 – 55	55
Decomposition temp. by DTA (°C)	185 – 190	190
Impact sensitivity (Nm)	5.6	6.3
Friction sensitivity	Insensitive up to 36 kg	Insensitive up to 36 kg
Flame temperature (K)	1660	1418

**Table 6. Results of vacuum stability test at 100 °C for 40 h**

Nomenclature of ingredients	Picrite CCC gas evolved (ml)	Resin CCC gas evolved (ml)
CCC sample (cm <sup>3</sup> /g)	0.15	0.12
NQ/M propellant (cm <sup>3</sup> /g)	0.91	0.92
Resin CCC + NQ/M Prop. (cm <sup>3</sup> /g)	0.90	0.88

**Table 7. Analysis results of resin-based CCC discs**

Ingredient	Analytical results (%)		Specified limits (%)
	I	II	
NC (12.6 % N)	72.25	72.49	72 ± 2
Cellulose + PVAc	26.74	26.54	28 ± 2
DPA	0.95	0.97	1.0 ± 0.1

## 3. RESULTS AND DISCUSSION

Initially, process parameters were established using PVAc dispersion in the selected formulation. In the first set of experiments, the temperature of the mould was chosen at 105 °C (based on its softening temperature) and the compacting pressure was varied from 3.9 MPa to 7.9 MPa with an increment of 1.0 MPa. The effect of compacting pressure on physico-mechanical properties such as density, tensile strength (TS), and elongation are presented in Table 2. It was observed that as the pressure increased, the TS increases and reaches an optimum value of 22.2 MPa at a pressure of 6.9 MPa, beyond which the TS decreased, which was attributed to the reduction in the free volume and increased association between PVAc and fibres of NC and cellulose, and subsequent bonding increased, resulting into increase in TS<sup>17</sup>. In the second set of experiments, compacting pressure was fixed at 6.9 MPa, while the temperature of mould was varied over the range 60–115 °C with an increment of 10 °C. The effect of mould temperature on physico-mechanical properties such as density, tensile strength and elongation is also presented in Table 2. Increasing trend of TS values was observed with increase in temperature due to increased mobility of polymer chains probably between its  $T_g$  and  $T_m$ <sup>18</sup>, reaching a threshold value at 105 °C. Beyond this temperature, the sample lost its original shape and deformed. This may be attributed to flowing of PVAc out of the matrix due to oversoftening<sup>18</sup>.

Using the above optimised process parameters (pressure: 6.9 MPa and temperature: 105 °C) effect of resin content, in the range 15-30 parts by weight was studied. Physico-mechanical properties of the disc obtained after varying resin content are presented in Table 3. It was observed that as the PVAc content increased, the density and TS also increased, reaching almost constant maximum value of TS (for 25 parts of PVAc: 26.1MPa and for 30 parts: 25.5 MPa) (Figs 3 and 4). Although different physical forces like dipole-dipole, ionic, and hydrogen bonding took place between NC, cellulose, and PVAc. A cumulative effect of hydrogen bonds between free-hydroxyl groups of cellulose, NC, and acetate groups of PVAc were more predominant, and hence, increase

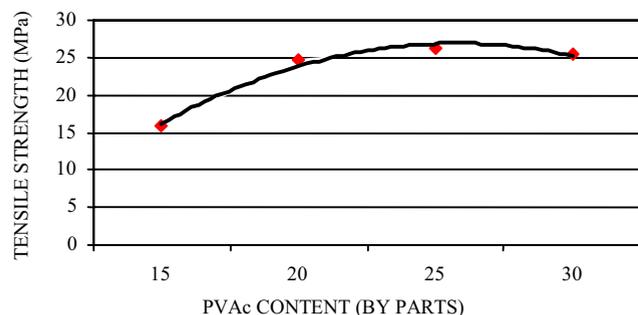


Figure 3. Effect of PVAc content on tensile strength.

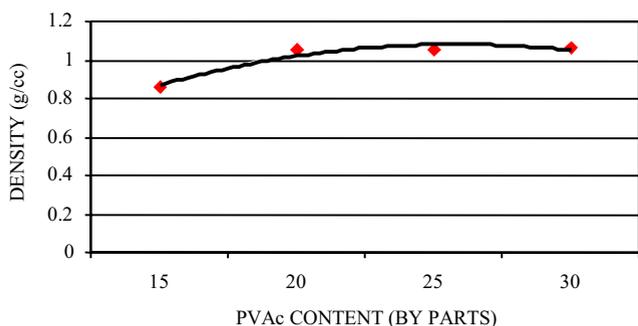


Figure 4. Effect of PVAc content on density.

in TS was attributed to the successive increase in hydrogen bonding between hydroxyl groups of cellulose, free-hydroxyl groups of NC, and acetate groups of PVAc<sup>16</sup>.

To finalise the formulation giving higher mechanical property along with desirable combustion characteristics, a few formulations were processed keeping the resin and DPA content constant and varying the quantity of NC and cellulose. Data on physico-mechanical properties and CV firing obtained on these discs is presented in Table 4. As the NC content decreased at the cost of increase in cellulose content, the density and TS increased (Figs 5 and 6) with marginal change in elongation which was attributed to the increased entangled fibrous structure throughout the matrix and their binding through resin particles. In the case of combustion parameters,  $dP/dt$  decreased while rise time increased with decrease in NC content. Considering the combustion characteristics of conventional CCCs ( $dP/dt$  of 45-55 MPa/ms and rise time of 4-7 ms), PVAc resin in the dispersion form appeared to be suitable when used in the formulation of

NC : Cellulose : DPA : PVAc as 83 : 17 : 1 : 20 parts by weight, which was also confirmed by dynamic evaluation. It was observed that the density is 1.1 g/cm<sup>3</sup> as against the theoretical density of 1.3 g/cm<sup>3</sup>. Data on stability, decomposition temperature and sensitivity of this formulation (Table 5) indicated that the stability of the CCC made using above formulation is comparable with that of picrite-based CCC<sup>3</sup>.

The results of dynamic firings indicated that the pressure and muzzle velocity obtained at -10 °C, 27 °C and 55 °C are well within the required limits. In addition, no debris/defects were observed in the breech-end as well as at the muzzle-end. The fired steel cups and bore of gun were clean. Less smoke was observed in crew compartment as well as at muzzle-end compared to the existing

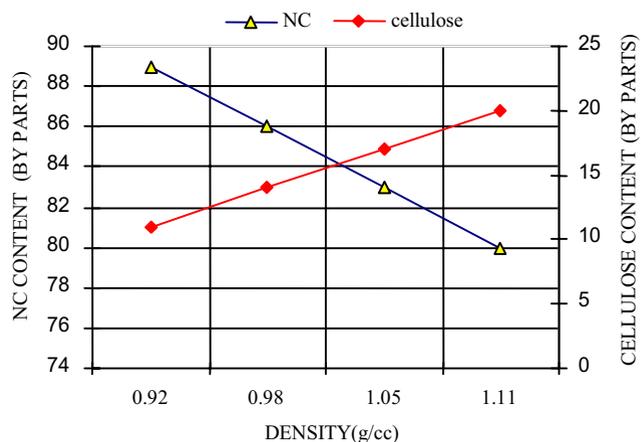


Figure 5. Effect of NC : Cellulose ratio on density of CCC.

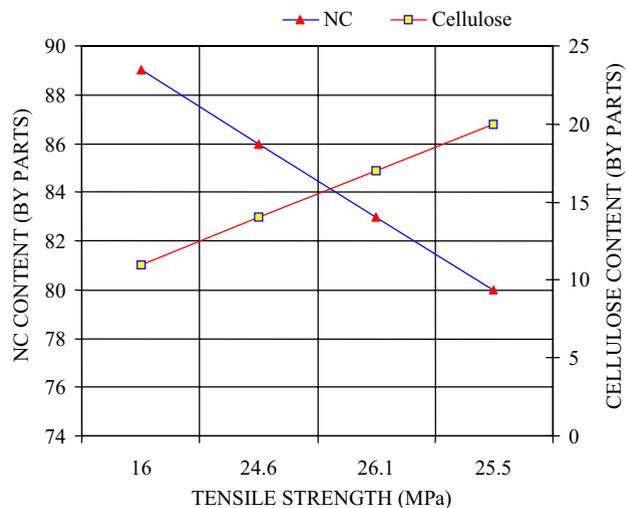


Figure 6. Effect of NC : Cellulose ratio on tensile strength.

CCC ammunition. The performance of resin-based CCC was better than the conventional CCCs.

#### 4. CONCLUSIONS

Incorporation of PVAc (dispersion) in the NC-cellulose-based combustible disc resulted into the improvement in mechanical strength when the discs were processed at compaction temperature of 105°C and compaction pressure of 6.9 MPa. At these process conditions, increase in resin content led to improvement in mechanical strength. At a fixed resin content, increase in NC content showed decrease in mechanical strength, while the combustibility of the formulations increased (as seen from rise in  $dP/dt$  and lower rise time).

Comparing the data on physico-mechanical and combustion characteristics for resin-based CCC and picrite-based CCC, it is quite evident that formulation containing NC : cellulose : DPA : PVAc (dispersion) in the ratio of 83 : 17 : 1 : 20 is suitable to achieve higher mechanical strength with better combustibility characteristics. Further, sensitivity and stability data generated on this formulation also revealed that PVAc resin-based CCC is more safe.

#### ACKNOWLEDGMENTS

The authors are thankful to Dr Haridwar Singh, the then Director, High Energy Materials Research Laboratory (HEMRL), Pune, for his valuable guidance. Thanks are also due to Dr Amarjit Singh, Associate Director and Dr P.B. Navale, Jt Director, HEMRL, Pune for their necessary help and encouragement to publish this work.

#### REFERENCES

- Sayal, R.K. & Narr, P.S. Study of brass obturator design for combustible cartridge case for 105 mm tank gun ammunition. *Def. Sci. J.*, 1997, **47**(3), 373-81.
- Kurulkar, G.R. Studies on combustible liners. Pune University, Pune, 1993. MSc Thesis.
- Kurulkar, G.R.; Syal, R.K. & Singh, H. Combustible cartridge case formulation and evaluation. *J. Ener. Mat.*, 1996 **14**, 127-49.
- Brasiques, A. & Maures, M. Spirally winding combustible paper tapes containing NC. US Patent 4, 649, 827. 17 March 1987.
- Boblinski, J. & Picard, J.P. Novel combustible cartridge case and process therefore. US Patent 3, 706, 280. 1972.
- Dutta, M.L. Report on visit to Isagchemie, Synthen, West Germany. 1986.
- Luebben, *et al.* Ammunition with protective surface layer and method of making same. US Patent 4, 363, 273. 14 December 1982.
- Haley, J.E. Design and manufacture of 155 mm modular propelling charges. US Army Armament Research & Development Center, Dover, New Jersey. Armtec Defence Products Co. 1984.
- Deluca, P. L. Manufacturing process for various shaped consumable ordance products. US Govt Report AD-A 121 656. 1982
- Maures, M. *et al.* Process for the manufacture of combustible articles by embossing combustible paper and combustible articles thus produces. US Patent 4, 705, 655.
- Barbets, R.I. Combustible cartridge case characterization. 1984, US Govt Report. AD-A 140664.
- Societe Nationale Des Poudres Et Explosifs, French Corporate Body, France. Mouldable compositions comprising polyvinyl nitrate. France Patent 1, 443, 289. August 1973.
- Remaly, *et al.* Felting process for making combustible cartridge cases. US Patent 3, 474, 702. 28 October 1969.
- Godfrey, J.N. & Myron, G. Cartridge cases from fibrous nitrocellulose and alkaline catalysed phenolic resin. US Patent 3, 260, 203. 12 July 1966.
- Beal, K.F. Combustible cartridge case and method of making same. US Patent 2, 982, 211. 2 May 1961.

16. Haley, J. Design and manufacture of 155 mm modular propellant charges. US Govt Report, 1984, AD-A 144273.
17. Seymour, R.B. & Carrher, C.E. Structure property relationships in polymers. Plenum Press, New York. pp. 22, 66, 160.
18. Scholz, H.J. Burning behaviour of combustible explosive charge case material in a closed vessel. *Internationale Jahrestagung*, 1983.
19. Gowarikar, V.R.; Vishwanathan, N.V. & Javade, Sreedhar. *In Polymer Science*. Wiley Eastern Ltd. & New Age International Ltd, New Delhi. pp. 156.

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