Study of an effect of promising cellulose components on the physico-mechanical properties and a burning rate of a combustible material for combustible cartridge cases produced according to the filtration casting technology

R V Fataliev¹, T A Eneikina¹, L A Kozlova¹, R F Gatina¹ and Yu M Mikhailov²

¹Federal State Enterprise, State Research Institute of Chemical Products, Kazan, Republic of Tatarstan, 1 Svetlaya Street, 420033, Russian Federation.
²Russian Academy of Sciences, Moscow, 14 Leninsky avenue, 119991, Russian Federation.

E-mail: fastish@mailgate.ru

Abstract. At present, cellulose and nitrocellulose components used in the field of ammunition are manufactured from a cotton linter or a wood. However, over the last decade the raw material characteristics, including for the nitrocellulose production for special purposes, have changed significantly both in connection with the loss of the traditional source of the cellulose raw material (the cotton linter) and with the deterioration of the quality of cotton cellulose. The new types of cellulose materials (a flax, a hemp, oats and etc.) have appeared on the market in due to the cotton deficit, intended for the special-purpose nitrocellulose. If we take into account the need to develop a component base based on the available domestic annually renewable sources of raw materials, then there is no doubt that the flax should be considered as a promising one.. In this connection, the possibility of an application of the flax pulp and NC based on it when manufacturing the combustible articles was investigated.

1. Introduction

If the possibility of making of powders based on NC manufactured from the flax pulp [1,2] has already been shown in a number of works previously, the possibility of an application of such material has not been tested for the combustible material. Two directions of an evaluation have been selected in this area. The first one is associated with the application of the cellulose and nitrocellulose fibrous material made of the flax in the combustible cartridge cases (CCC), manufactured according to the filtration casting technology. The second one is associated with the use of partially substituted flax-based cellulose nitrates. In this connection, the effect of these components on the physico-mechanical properties and a burning rate of CCC material were investigated. The features of the composite material are associated with the technology of the product manufacture. In particular, the filtration casting method involves the use of the cellulose in the form of a fibre and this is associated with the uniqueness of its properties that are manifested in the ability to form strong interfibre bonds.
2. Effect of the flax pulp and NC raw materials on the mechanical strength of products

At first, the effect of the flax pulp and NC raw materials of the fibrous form on the mechanical strength of products is considered.

2.1. A geometrical dimensions of fibres

For a determination of the geometrical dimensions of fibres, 50 fibres of partially substituted cotton cellulose nitrates (PSNC) and the flax cellulose nitrates (N = 7.6 %) were isolated, the replicas were made on a paper, after that the average fibre length was calculated by the program. The results are given in Table 1. The reference data for a length and a thickness for the wood pulp were taken, since the fibre had the form of a strongly twisted ball. The thickness and the nature of the fibres were determined using the microscope at 100x magnification.

| Name of material                        | An average length of a fibre (L, mm) | An average thickness of a fibre (d, mm) | A characteristic ratio (L/d) | An appearance of a fibre | A freeness value (°ShR) |
|----------------------------------------|-------------------------------------|----------------------------------------|-----------------------------|--------------------------|------------------------|
| Partially substituted cotton cellulose | 0.70                                | 0.0216                                 | 32.4                        | Wavy, curved             | 10                     |
| Flax pulp                              | 0.70                                | 0.0308                                 | 22.73                       | straight, slightly wavy  | 10                     |
| Wood pulp of E-2 mark                  | 1.79                                | 0.020                                  | 89.5                        | strongly twisted, curved | 43                     |

* Shopper-Rigler degree

A comparison of the fibres of a cotton, a flax and a wood pulps based on the main parameters are presented in Table 2.

| Name of material                        | An average geometrical dimensions of a fibre, mm: length diameter | Density (g/cm³) | An interfibre bonding strength, MPa at a reduction ratio (°ShR) | An average tension strength (MPa) | A tensile elongation, ε (%) | Stress-strain modul us |
|----------------------------------------|---------------------------------------------------------------|-----------------|---------------------------------------------------------------|---------------------------------|---------------------------|------------------------|
| Cotton                                 | 20÷25 0.039                                                  | 1.567           | 1.49 1.61 1.75                                               | 485.7                           | 8÷10                      | 5÷10                   |
| Flax                                   | 20÷25 0.031                                                  | 1.510           | 1.38 1.58 1.70                                               | 842.9                           | 2÷3                       | 30÷50                  |
| Bleached sulphate wood savwood        | 1.7÷1.8 0.023                                               | 1.560           | 2.18 2.30 2.40                                               | 520                             | 10÷20                     | 6÷11                   |
| Bleached sulphate wood hardwood       | 2.5÷3.0 0.017                                               | 1.540           | 1.61 1.78 2.30                                               | -                               | 10÷20                     | -                      |

A comparison of the properties, presented in Table 2, shows that in terms of the interfibre bond strength (a cohesiveness) the flax is inferior to the cotton and the wood, although it surpasses them in tensile strength. The melt of high explosive acts as a fuel-binding matrix in the standard combustible material (CM) of the filtration casting, but its own strength is only 3÷5 MPa due to the cohesive interaction. The actual practice of the use of CCC of the filtration casting has shown that the cellulose
plays the dominating role in ensuring the required physico-mechanical properties of CM. In this connection, it is obvious that a component is needed, which, by intensifying a burning process, would simultaneously have paper-forming properties similar to the cellulose. The partially substituted NC (PSNC) could be presented the greatest interest in this plan, combining a higher potential in comparison with the cellulose with the paper-forming properties due to the presence of the sufficient amount of OH-groups in a molecule, that are responsible for this parameter [1]. In Table 3 the main characteristics of PSNC are given in comparison with «2P» and «1Pl» pyroxylin.

| Table 3. The characteristics of cellulose nitrates |
|--------------------------------------------------|
| Name of material | Volume concentration of nitrogen oxide, (ml NO/g) | Viscosity, (°E°) | Ether alcohol solubility, (°), no less than |
|------------------|--------------------------------------------------|------------------|-----------------------------------|
| 2P (l) based on a flax | 199.8 | 12.5 | 11.8 | 98.6 |
| (PSNC) | 121.4 | 7.6 | 23÷24 | not soluble |
| 2P made of a wood paper | 197.9 | 12.38 | 7.8 | 96.5 |
| (standard) | | | | |
| 1Pl made of a cotton cellulose | 212.1 | 13.27 | 5.1 | 9.2 |

*aEngler degree

2.2. The CM samples were produced according to the filtration casting technology
The samples of CM were produced according to the filtration casting technology using 2P (l) pyroxylin manufactured from the flax pulp. The test results are given in Tables 4 and 5.

| Table 4. The samples of the combustible material of CCC |
|--------------------------------------------------------|
| Name of parameter | Content, % by mass | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|------------------|--------------------|---------|---------|---------|---------|---------|
| 2P pyroxylin from the cotton cellulose | - | - | 57 | 57 | 40 |
| 2P (l) pyroxylin from the flax pulp | 57 | 57 | - | - | - |
| 1Pl pyroxylin from the cotton cellulose | - | - | - | - | 40 |
| The flax pulp | - | Y | Y | - | - |
| The wood pulp of E-2 mark | Y | - | - | Y | - |
| High explosive | X | X | X | - | - |
| Polyvinylacetate | - | - | - | - | 20 |

| Table 5. The test results of CM samples for CCC |
|------------------------------------------------|
| Name of parameter | Parameter | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|------------------|-----------|---------|---------|---------|---------|---------|
| Density (g/cm³) | 0.9 | 0.92 | 0.91 | 0.95 | 1.12 |
| Tensile strength (MPa) | 10÷11 | 4÷5 | 7÷8 | 10÷12 | 7÷7.5 |
| Elongation (%) | 5.0 | 4.0 | 3.5 | 5.0 | 1.0 |
| Delay time of an ignition, sec | 0.0085 | 0.0088 | 0.0090 | 0.0087 | 0.0015 |
| Force, F, average (tfm/kg) | 67.4 | 67.0 | 66.5 | 67.6 | 66.0 |
| Burning rate, U1 · 10⁹ (m/sec) at pressure of 100 MPa | 0.68 | 0.68 | 0.69 | 0.70 | 0.73 |

Note: 1. All materials are not lacquered. 2. The loading density is 0.126 g/cm³. 3. The requirements
for CCC for mortar rounds: - a tensile strength, MPa, no less than 8.0; - a burning rate at P = 100 MPa, m/sec, no less than 0.70; - a delay time of an ignition, sec, no more than 0.050.

It follows from the data of Table 5 that CM of the standard formulation (sample 4) has the greatest strength, which is based on the wood pulp of «E-2» mark, and it is consistent with the data from Table 2 in accordance with which the greatest interfibre bond strength is characteristic for the wood types of cellulosics. The samples 1 and 3 have also quite high strength of CM, although it is less than that of sample 4. The identity of properties of samples 1 and 3 based on the main parameters (the mechanical strength, the burning characteristics) indicates the equivalence of the use of pyroxylins based on the flax and the cotton cellulose. Moreover, only samples 1 and 3 satisfy the main requirements for a strength, a burning rate and a delay time of an ignition of CM of CCC. The sample 2 has the lowest mechanical strength, equal to 4÷5 MPa, which contains the flax cellulose instead of the wood pulp as a reinforcing component. A severe drop in strength (∼ in twice) demonstrates the lower reinforcing properties of the flax pulp and it confirms that the main purpose of NC in the composition of the material, manufactured according to the filtration casting technology, is primarily the energetic base and not the reinforcing one. The sample 5 has the smallest delay time of the ignition: it ignites faster in six times than sample 4 manufactured from the standard material due to the presence of «1Pl» pyroxylin with a high nitrogen content. However, it is a quite brittle and it must be because of the lack of the cellulose fibres.

2.3. Model double base samples and certain volume concentration
The model double base samples based on the cellulose and PVA, which is recommended for use as the binder in thermostable CM, were manufactured for a confirmation of the dominating influence of the type of the cellulose fibre on the material strength [7]. The test results of samples 6, 7 and 8, given in Table 6, confirm the conclusion, drawn above, about the best reinforcing properties of the wood pulp in comparison with the cotton and the flax cellulose. It also confirms that the cellulose elimination from the CM composition dramatically decreases its mechanical strength (samples 9 and 10).

| Name of parameter | Sample 6 | Sample 7 | Sample 8 | Sample 9 | Sample 10 |
|-------------------|----------|----------|----------|----------|-----------|
| PVA, % by mass (according to the introduction) | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 |
| Cellulose, (%) by mass (according to the introduction) | 75.0 | 75.0 | 75.0 | - | - |
| (flax) | (cotton) | (wood) |
| PSNC (cotton) | - | - | - | 75.0 | - |
| 2P pyroxylin (flax) | - | - | - | - | 75.0 |
| Tensile strength (MPa) | 9.5 | 11.5 | 13.5 | 4.5 | 7.2 |
| (9.3÷9.7) | (12.0÷12.7) | (4.3÷4.8) | (6.7÷8.7) | |
| Elongation (%) | 7.0 | 7.0 | 0.7 | 3.0 | 2.0 |
| The volume fraction of the cellulose, at which the percolating cluster is formed (%), with the characteristics from Table 2 | 2.64 | 1.85 | 0.67 | - | - |
| The volume fraction of the cellulose, at which the percolating cluster is formed (%) under the conditions of the similar freeness value (a length is 1.79 mm) | 1.03 | 0.72 | 0.67 | - | - |
The observing effect is explained in the following way. The percolating cluster forms in case of the homogeneous distribution of the fibrous filler in the matrix volume at its certain volume concentration ($V_f$). The volume concentration of the particles of the cylindrical form $V_f$ is determined according to the equation (1) [8]:

$$V_f = \frac{0.6}{r},$$

where $r = L/d$, $L$ – a fibre length, $d$ – a fibre diameter.

The $V_f$ parameters were calculated according to the data from Table 1 and they are given in Table 6. In accordance with the calculations the percolating cluster for the wood pulp is formed at its volume content of 0.67 % and for the cotton and the flax cellulose at its volume content of 1.85 and 2.64 %, respectively, i.e. there is a clear tendency of a dependence of the mechanical strength on its concentration. Therefore, the reinforcing properties are weaker with the similar mass introduction for the fibres of the flax pulp that have the lowest value of the axial (characteristic) ratio than the fibres of the wood and the cotton celluloses. If we compare $V_f$ values of celluloses at the similar freeness value ($L = 1.79$ mm), then the parameter of the volume concentration $V_f$, of the cotton cellulose will be near to the value of the volume concentration of the wood pulp and $V_f$ value of the flax pulp is lower than $\approx 53 \%$.

2.4 Using NC with a low nitrogen content for combustible material manufacturing

The samples of the combustible material were manufactured using partially substituted cotton cellulose nitrates (PSNC) instead of the cellulose according to the filtration casting technology (Table 7). The obtained test results are given in Table 7. At the laboratory scale, the CM production reproduces the technological process of RCB manufacturing in experimental-industrial conditions and it is carried out according to the methodology of “GosNIIKhP” FSE. It follows from the data of Table 7 that sample 2 of the standard formulation has slightly greater strength and elongation. However, the burning rate (by about 16 %) and the ignitable ability (by about 3÷4 times) of samples 1 and 3 based on PSNC increased.

| Name of parameter                  | Content, % by mass (according to the introduction) |
|------------------------------------|----------------------------------------------------|
|                                    | Sample 1   | Sample 2 (standard) | Sample 3 |
| 2P pyroxylin                       | Y          | Y                   | Y        |
| LNNC                               | 20         | -                   | 10       |
| Wood pulp of E-2 mark              | -          | 20                  | 10       |
| High explosive                     | X          | X                   | X        |
| Density (g/cm$^3$)                 | 0.91       | 0.95                | 0.94     |
| Tensile strength (MPa)             | 8÷9        | 10÷12               | 10÷11    |
| Elongation, (%)                    | 3.5        | 5.0                 | 4.7      |
| Delay time of an ignition, sec     | 0.0021     | 0.0087              | 0.0032   |
| Force, F, average (tfm/kg)         | 72.9       | 67.6                | 69.7     |
| Burning rate, $U_1 \cdot 10^6$, (m/sec) at a pressure of | 0.80       | 0.70                | 0.76     |
100 MPa
Note: 1. All materials are not lacquered. 2. The loading density is 0.126 g/cm³. 3. The requirements for CCC for mortar rounds: - a tensile strength, MPa, no less than 8.0; - a burning rate at P = 100 MPa, m/sec, no less than 0.7; - a delay time of an ignition, sec, no more than 0.0050.

The decrease in strength is probably associated with the replacement of the wood pulp by NC with low nitrogen content, having worse paper-forming (reinforcing) properties. Taking into account that the physico-mechanical properties of samples 1 and 3 decreased insignificantly and they are at the acceptable level for CCC, then it is possible to recommend a partial substitution of the cellulose for NC with low nitrogen content as a part of CCC for mortar rounds for providing the completeness of combustion.

3. Conclusion:
The application of flax as the alternative component instead of the wood and the cotton celluloses in CCC production according to the filtration casting technology is possible and it slightly decreases the physico-mechanical properties at the certain freeness value of the fibre. The possibility of NC application is shown that were obtained from the flax cellulose in the course of manufacturing of combustible products according to the filtration casting technology with maintaining the physico-mechanical properties and the burning rate of the material. It is advisable to use partially substituted NC based on the wood and the cotton celluloses (the content of nitrogen oxides is no more than 100 ml NO/g) instead of cellulose in connection with increasing of the energetic characteristics of CM with the satisfactory mechanical strength.

References
[1] Shakhmima E V 2005 The production technology of the industrial cellulose nitrates marks manufactured from the flax, Phd (Kazan city: “GosNIIKhP” FSE) (in Russian)
[2] Budaeva V V 2009 Proceedings of All-Russian Scientific-Technological and Methodic Conf. Modern Problems of Special Industrial Chemistry (Kazan city: Kazan State Technological University) pp 275–81 (in Russian)
[3] Komarov V I et al. 2005 Technology of Pulp and Paper Production, vol. 2, Production of Paper and Cardboard (St. Petersburg: Polytechnics) p 423 (in Russian)
[4] Berlin A A 2009 Polymer Composite Materials: Structure, Properties, Technology (St. Petersburg: Professija) p 560 (in Russian)
[5] Kozubov P M 1976 The Diagnostic Properties of the Wood and Cellulose Fibres (Petrozavodsk city: CRI of Paper) p 146 (in Russian)
[6] Gess K G 1934 Chemistry of Cellulose and its Satellites (Leningrad: ORTI – Goskhimizdat) p 620 (in Russian)
[7] Eneikina T A 2015 Boepripasy XXI Vek. 2 28–37 (in Russian)
[8] Yudin V E and Svetlichnyi V M 2009 Ross. Khim. Zh. 53 (4) 75–85 (in Russian)