# Shrinkage in Propellant Manufactured by Solvent Process 

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#### Abstract

The propellant manufacturers select the dimensions of die-pin for extrusion of dough by trial and error method based on their experience. This paper presents a general equation applicable for any propellant composition processed by solvent process, in any shape, i.e., cord, monotubular or the multitubular. To illustrate the relationship, calculation for outer radius for a few typical single-base propellants is given.


## 1. INTRODUCTION

In the solvent process for manufacture of propellant, nitrocellulose (NC) is gelatinised to desired consistency with the help of the solvent. The solvent is removed by drying process after the extrusion of gelatinised mass (dough). In this process, as the solvent leaves the system-the solid ingredients (NC, etc), non-volatile materials (plasticisers, modifiers, etc), and the volatile solvents-the dimensions of extruded material shrink.

By and large, all the propellant manufacturers are required to manufacture the propellants with a given finished dimensions and density. As such, they are supposed to extrude the dough at such dimensions which after removal of solvent, i.e., after shrinkage, will conform to rigid physical specifications. Even though the art of propellant manufacture is more than a century old (Kays ${ }^{1}$, Urbanski ${ }^{2}$ and Ball ${ }^{3}$ describe the state-of-art adequately, most of the propellant manufacturers select the

[^0]dimensions of die-pin for extrusion of dough by trial and error method based on their experiences. This paper presents an alternative approach to the problem of die-pin dimensions through theoretical calculations.

### 1.1 Theory

Let $\Sigma V_{s}$ be the summation of individual volumes of non-volatile components, $\Sigma V_{1}$ be the summation of individual volumes of volatile solvent taken for kneading, $\Sigma M_{s}$ be the summation of individual masses of non-volatile components, and $\Sigma M_{1}$ be the summation of individual masses of volatile solvents taken for kneading.

The calculated density of dry propellant is given by

$$
\begin{equation*}
d=\frac{\Sigma M_{s}}{\Sigma V_{s}} \tag{1}
\end{equation*}
$$

The calculated density of green (wet) propellant is given by

$$
\begin{equation*}
\frac{\Sigma\left(M_{s}+M_{1}\right)}{\Sigma\left(V_{s}+V_{1}\right)} \tag{2}
\end{equation*}
$$

and the ratio of dry mass to wet mass is given by

$$
\begin{equation*}
A=\frac{\Sigma M_{s}}{\Sigma\left(M_{s}+M_{1}\right)} \tag{3}
\end{equation*}
$$

If $W$ is the mass of unit length of green propellant, then the mass of propellant after drying is equal to $W A$. But the mass of unit length of dried propellant is given by

$$
\begin{equation*}
\pi\left(R^{2}-n R_{1}^{2}\right)\left(\frac{100-p}{100}-\right)^{d} \tag{4}
\end{equation*}
$$

where $p$ is the per cent porosity, $R$ is the outer radius, $R_{1}$ the inner radius, and $n$ the number of holes.

That is

$$
\begin{equation*}
\frac{\pi(100-p)}{100} d\left(R^{2}-n R_{1}^{2}\right)=W A \tag{5}
\end{equation*}
$$

or

$$
\begin{equation*}
R=\left(\frac{100 W A}{\pi d(100-p)}+n R_{1}^{2}\right)^{1 / 2} \tag{6}
\end{equation*}
$$

Under the extrusion conditions, let the flow of dough (green material) be assumed to be a streamlined one. Then the diameter of strands formed during the extrusion will be the same as the diameter of the die hole. This gives the mass of unit length of propellant (green) as

$$
W=\pi\left(r_{O D}^{2}-n r_{I D}^{2}\right) \Sigma\left(M_{s}+M_{1}\right) / \Sigma\left(V_{s}+V_{1}\right)
$$

where $r_{O D}$ is the radius of the die hole, and $r_{I D}$ is the radius of pins.
Substituting the values of $W$ and $A$ in Eqn. (5) we get

$$
\begin{align*}
& R=\left[\frac{100 \pi\left(r_{O D}^{2}-n r_{I D}^{2}\right) \frac{\Sigma\left(M_{s}+M_{1}\right) \Sigma M_{s}}{\Sigma\left(V_{s}+M_{1}\right) \Sigma\left(M_{s}+M_{1}\right)}}{\pi d(100-p)}+n R_{1}^{2}\right] \\
& =\left(\frac{100\left(r_{O D}^{2}-n r_{I D}^{2}\right) \Sigma M_{s}}{d(100-p) \Sigma\left(V_{s}+V_{1}\right)}+n R_{1}^{2}\right)^{1 / 2} \tag{7}
\end{align*}
$$

Substituting the value of $d$ from Eqn. (1)

$$
\left.\begin{array}{rl}
R & =\left(\frac{100\left(r_{O D}^{2}-n r_{I D}^{2}\right) \Sigma M_{s}}{\sum M_{s}} \frac{\sum V_{s}}{\sum(100-p) \Sigma\left(V_{s}+V_{1}\right)}+n R_{I}^{2}\right)^{1 / 2} \\
& =\left(\frac{100\left(r_{O D}^{2}-n r_{I D}^{2}\right) \Sigma V_{s}}{(100-p) \Sigma\left(V_{s}+V_{1}\right)}+n R_{1}^{2}\right. \tag{8}
\end{array}\right)^{1 / 2},
$$

In Eqn. (8) terms $R$ and $R_{1}$ (dimensions of propellant) or $r_{O D}$ and $r_{I D}$ (dimensions of die-pin) are unknown. In order to solve the above equation, approximation is used as follows.

In comparison to $R$, both the radius $R_{1}$ and $r_{I D}$ are very small and hence for first order computation it is assumed that

$$
R_{1} \approx r_{I D}
$$

Substituting the value of $\boldsymbol{R}_{1}$ in Eqn.(8)

$$
\begin{equation*}
R=\left(\frac{100\left(r_{O D}^{2}-n r_{I D}^{2}\right) \Sigma V_{s}}{(100-p) \Sigma\left(V_{s}+V_{1}\right)}+n r_{I D}^{2}\right)^{1 / 2} \tag{9}
\end{equation*}
$$

or

$$
\begin{equation*}
R=\left(\frac{100\left(r_{O D}^{2}-n R_{1}^{2} \Sigma V_{s}\right.}{(100-p) \Sigma\left(V_{s}+V_{1}\right)}+n R_{1}^{2}\right)^{1 / 2} \tag{10}
\end{equation*}
$$

Equations (9) and (10) give a direct relationship between the radius (outer) of propellant under consideration and the process conditions (dimensions of die-pin and solvents taken for gelatinisation), and can be used for calculating the shrinkage and die diameters.

Since, in the proposed relationship, $\Sigma V_{s}$ represents the volumes of non-volatile components in a propellant composition, this relationship is valid for all types of propellant compositions. Further one can use this for cord, monotubular or the multitubular shapes by giving an appropriate value to $\boldsymbol{n}$, i.e., $\boldsymbol{n}$ is $\mathbf{0}$ for cord, $\boldsymbol{n}$ is 1 for monotubular, $\boldsymbol{n}$ is $\mathbf{7}$ for heptatubular, and so on.

## 2. EXAMPLES

The following examples illustrate the calculation for outer radius for a few typical single-base propellant compositions.

### 2.1 Example 1

Let the composition of dough be as shown in Table 1. The dough is extruded through a die-pin assembly $6.88 / 3.69 / 0.73 / 0.73 \mathrm{~mm}$ in heptatubular shape, (i.e., $n$ is 7). Porosity of the propellant after drying is 2 per cent (i.e., $P$ is 2 ). Also $\Sigma V_{s}=61.31 \mathrm{l}$, and $\Sigma\left(V_{s}+V_{1}\right)=143.44$ 1. Substituting these values in Eqn. (9), we get $R=2.38 \mathrm{~mm}$. This compares favourably with the experimentally found value of 2.36 mm .

Table 1. Composition of the wet propellant mass for example 1

| Ingredients | Density <br> $(\mathrm{g} / \mathrm{cc})$ | Mass* <br> $(\mathrm{kg})$ | Voume <br> $(\mathrm{l})$ |
| :--- | :---: | :---: | :---: |
| Nitrocellulose (dry mass) | 1.66 | 88.4 | 53.25 |
| Diphenylamine | 1.16 | 0.98 | 0.845 |
| Dibutylphthalate | 1.04 | 1.47 | 1.41 |
| Dinitrotoluene | 1.32 | 7.37 | 5.58 |
| Potassium nitrate | 2.66 | 0.60 | 0.225 |
| Ether | 0.71 | 35.5 | 50.0 |
| Alcohol and water | 0.80 | 25.70 | 32.13 |

[^1]
### 2.2 Example 2

The composition of dough in this example is shown in Table 2. The dough is extruded through a die-pin $1.95 / 0.3 \mathrm{~mm}$ in monotubular shape (i.e., $n$ is 1 ). Porosity of propellant after drying is 4 per cent (i.e., $P$ is 4$)$. Also $\Sigma V_{s}=651$, and $\Sigma\left(V_{s}+\right.$ $\left.V_{1}\right)=199.25$ 1. Substituting these values in Eqn. (9), we get $R=0.58 \mathrm{~mm}$ which compares with the experimental value of 0.62 mm .

Table 2. Composition of the dough for example 2

| Ingredients | Composition <br> (parts by mass) | Density <br> $(\mathrm{g} / \mathrm{cc})$ | Mass <br> $(\mathrm{kg})$ | Volume <br> $(\mathrm{l})$ |
| :--- | :---: | :---: | :---: | :---: |
| Nitrocellulose | 98.0 | 1.66 | 105.0 | 63.25 |
| Diphenylamine | 0.5 | 1.16 | 0.54 | 0.46 |
| Centralite | 0.5 | 1.12 | 0.54 | 0.48 |
| Potassium bi-tartrate | 1.0 | 1.96 | 1.60 | 0.81 |
| Ether | 51.69 | 0.71 | 55.38 | 78.0 |
| Alcohol and water | 42.0 | 0.8 | 45.0 | 56.25 |

### 2.3 Example 3

Let the composition of dough be as shown in Table 3. The dough is extruded through a die 1.3 mm in cord shape (i.e., $\boldsymbol{n}$ is $\mathbf{0}$ ). Porosity of propellant after drying is 4 per cent (i.e., $P$ is 4 ). Also $\Sigma V_{s}=891$, and $\Sigma\left(V_{s}+V_{1}\right)=2191$. Substituting the values in Eqn. (9), we get $R=0.42 \mathrm{~mm}$, which compares with the experimental value of 0.43 mm .

Table 3. Composition of the dough for example 3

| Components | Composition <br> (parts by mass) | Density <br> (g/cc) | Mass <br> $(\mathbf{k g})$ | Volume <br> (l) |
| :--- | :---: | :---: | :---: | :---: |
| Nitrocellulose | 91 | 1.66 | 136.53 | 82.25 |
| Diethylphthalate | 2 | 1.12 | 2.90 | - |
| Carbamite | 2 | 1.12 | 2.90 | 5.18 |
| Cuprous oxide | 1.5 | 6.0 | 2.2 | 0.37 |
| Leadphthalate | 3 | 6.8 | 4.35 | 0.64 |
| Potassium nitrate | 1 | 2.1 | 1.18 | 0.56 |
| Ether | 36 | 0.71 | 54.0 | 76.0 |
| Alcohol and water | 28.8 | 0.8 | 43.2 | 54.0 |

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## REFERENCES

1. Kays, Saymour, M. Encyclopedia of explosives and related items (PATR-2700), Vol. 8 : US Army Armament Research and Development Command, New Jersey, 1978. pp. 403-473.
2. Urbanski, T. Chemistry and technology of explosives, Vol. 3 : Pergamon Press, New York, 1967. pp. 528-688.
3. Ball, A.M., Solid propellants, Part I. AMCP 706-175, September 1964. pp. 10-110.
4. Dean, John, A.,(Ed). Lange's hand book of chemistry, Ed. 12. McGraw-Hill, New York, 1979. pp. 7.54-7.93.

[^0]:    Received 15 May 1989, revised 28 November 1989.

[^1]:    * Composition of dough (parts by mass)

