THE EFFECT OF PROCESSING VARIABLES ON THE "INTERNAL SLIP FLOW" OF A TRIPLE BASE GUN PROPELLANT DOUGH

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ABSTRACT

The rheological behaviour of triple base gun propellant doughs of N and NQ types was measured with an extrusion rheometer at temperatures of 29°C, 30°C and 45°C, using slit and capillary dies. The propellant doughs were made from two grades of nitrocellulose, and from picrite obtained from two sources. Acetone/water mixtures and acetone/ethanol mixtures were used as processing solvents. Most of the processing variables had little effect on flow behaviour. It was found that a type of internal slip occurred in the dough at a shear stress of about 60 kPa, and this had a significant effect on flow behaviour.

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1. INTRODUCTION

N and NQ type triple base gun propellants are used in the UK designed Abbot Mk 2 105 mm ammunition. The manufacturing processes specified in the UK for these propellants involve some differences from processes used in current Australian propellant production. In particular, the solvents used for N and NQ propellants are acetone/water mixtures, instead of the more common acetone/ethanol or ethyl acetate/ethanol mixtures. Another difference is the type of picrite used. Picrite used in UK production is obtained from ROF Bishopton, whereas in Australia picrite from both Bishopton and from the FRG (Nigu-Chemie) is currently used in the manufacture of triple base propellants. The only known study of the effect of processing variables on rheology of N and NQ type propellants did not address these issues, as it dealt mainly with the effect of changes in total solvent level and temperature (ref. 1).

This paper reports work done to determine the effect of solvent water level and picrite type on the rheological properties of the propellant doughs, and also the discovery of an unusual type of flow behaviour in the doughs. Work done on assessing the effect of processing changes on propellant manufacture, as well as the effects on ballistic and mechanical properties of the propellants, will be reported separately (ref. 2).

2. EXPERIMENTAL

2.1 Materials

The formulations of N and NQ propellants are given in Table 1. The nitrocellulose (NC) used was either directly nitrated to 13.0%N (designated Grade F), or made from a blend of 12.6%N and 13.4%N NC with a nitrogen content of 13.15% (designated Grade Cl). The two types of picrite used were designated Bishopton and Nigu-Chemie. The Bishopton picrite was more needle-like than the Nigu-Chemie picrite.

The propellants were manufactured by the standard procedure, which is described in detail in another publication (ref. 2). Two series of propellants were made; one in a 5 kg mixer to produce samples for ballistic, physical and mechanical testing as well as doughs for rheological testing in capillary dies, and a second series in a 1 kg mixer to produce doughs for rheological testing in slit dies. The processing, ballistic and mechanical properties are described in reference 2.

The standard processing solvent for N and NQ propellants is acetone diluted with water. The water concentration is normally 8%, but the effect of water content was studied by using solvents containing 0 and 14% water as well. For comparison, acetone/ethanol mixtures were also used. The total solvent level had to be varied for each lot of ingredients or processing conditions to produce acceptable quality doughs. Details of all the propellants manufactured are given in Table 2.
TABLE 1: PROPELLANT FORMULATIONS

<table>
<thead>
<tr>
<th>Ingredient level (weight/cent)</th>
<th>N</th>
<th>NQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose</td>
<td>18.90</td>
<td>20.70</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>18.60</td>
<td>20.50</td>
</tr>
<tr>
<td>Picrite (nitroguanidine)</td>
<td>54.70</td>
<td>54.70</td>
</tr>
<tr>
<td>Ethyl centralite</td>
<td>7.25</td>
<td>3.58</td>
</tr>
<tr>
<td>Potassium sulphate</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Residual solvent</td>
<td>0.25</td>
<td>0.22</td>
</tr>
</tbody>
</table>

2.2 Rheological testing

Rheological testing was carried out in an extrusion rheometer consisting of a water jacketed barrel with dimensions 32 mm internal diameter and 180 mm long, with a ram driven at constant rates by an Instron machine. There was provision for various types of dies in water jacketed holders to be attached to the bottom of the barrel. Two die configurations were used in this work: capillary dies, and a slit die.

The capillary dies had diameters 0.91 mm and 3.27 mm, and length/diameter ratios of 10:1 and 20:1, giving 4 dies in all. They were made from thin walled brass tubing glued inside aluminium blanks. Aluminium and brass were used instead of stainless steel to improve the conduction of heat generated by viscous dissipation at high shear rates. The pressure required to extrude dough through the capillaries was measured by a transducer mounted in the barrel just above the die entrance.

The size of the slit die was 0.98 mm thick, 10.0 mm wide and 30.3 mm long. Two miniature pressure transducers were flush mounted along the centreline in the wall of the slit at distances of 10.1 mm and 24.9 mm from the slit entrance.

Shear stress and shear rate at the die walls were calculated from the standard formulae:

For capillary dies,

\[ \sigma_a = \frac{P \cdot D}{4L} \]  \hspace{1cm} (1)

\[ \dot{\gamma}_a = \frac{32Q}{nD^3} \]  \hspace{1cm} (2)

where \( \sigma_a \) and \( \dot{\gamma}_a \) are the apparent shear stress and shear rate respectively, \( P \) is the pressure drop along a die of diameter \( D \) and length \( L \), and \( Q \) is the volume flow rate of propellant. For slit dies
\[ \sigma_a = \frac{P\cdot h}{2L} \quad (3) \]

\[ \dot{\gamma}_a = \frac{6Q}{wh^3} \quad (4) \]

where \( h \) and \( w \) are the slit thickness and width respectively, and \( P \) is the difference in pressure between the two transducers separated by a distance \( L \) along the die.

### TABLE 2. DETAILS OF PROPELLANT MANUFACTURE

<table>
<thead>
<tr>
<th>Solvent type (^a)</th>
<th>Ratio</th>
<th>Picrite type (^b)</th>
<th>GP Solvent No.</th>
<th>(%) (^3)</th>
<th>NC Solvent No.</th>
<th>(%)</th>
<th>NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>For capillary measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>NIGU</td>
<td>659</td>
<td>80</td>
<td>F</td>
<td>652</td>
<td>70</td>
</tr>
<tr>
<td>A/W</td>
<td>92/8</td>
<td>NIGU</td>
<td>653 647</td>
<td>97/110</td>
<td>F/C1</td>
<td>646</td>
<td>90</td>
</tr>
<tr>
<td>A/W</td>
<td>92/8</td>
<td>BISH</td>
<td>658</td>
<td>102</td>
<td>F/C1</td>
<td>651</td>
<td>94</td>
</tr>
<tr>
<td>A/W</td>
<td>86/14</td>
<td>NIGU</td>
<td>655 650</td>
<td>102/115</td>
<td>F/C1</td>
<td>648</td>
<td>95</td>
</tr>
<tr>
<td>E/A</td>
<td>1/1</td>
<td>NIGU</td>
<td>662</td>
<td>104</td>
<td>F</td>
<td>660</td>
<td>98</td>
</tr>
<tr>
<td>E/A</td>
<td>1.5/1</td>
<td>NIGU</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>657</td>
<td>120</td>
</tr>
<tr>
<td>For slit die measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A/W</td>
<td>92/8</td>
<td>NIGU</td>
<td>733 728</td>
<td>105/110</td>
<td>F/C1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A/W</td>
<td>92/8</td>
<td>BISH</td>
<td>734 729</td>
<td>114/123</td>
<td>F/C1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes:
(1) \( A = \) acetone, \( W = \) water, \( E = \) ethanol
(2) NIGU refers to Nigu-Chemie and BISH refers to Bishopton picrites.
(3) The solvent level is weight percentage of the weight of NC.
(4) The Grade F NC is directly nitrated to a nitrogen level of 13.0%, and the Grade C1 NC is made up of a blend of NCs with nitrogen levels of 12.6% and 13.4% to give an average nitrogen level of 13.15%.

The apparent shear rates were corrected for non-Newtonian velocity profiles in the die by applying the Rabinowitsch correction, see Appendix I. The apparent shear stresses calculated for the capillary dies were corrected for pressure losses in the entrance region of the die by using the Bagley correction, see Appendix II. The stresses calculated for the slit die do
not require correction because the pressure drop in the die is measured directly.

3. RESULTS

3.1 Effect of processing variables on flow curves

This work has confirmed the reputation of NQ and N as most forgiving propellants to manufacture, because the rheological behaviour was relatively insensitive to most of the processing variables studied.

The effects of all the variables except temperature will be illustrated using the capillary data because of the greater shear rate range covered, and the effect of temperature will be illustrated using the slit die data. The data from the slit and capillary die cannot be compared directly because a 1 kg mixer was used for the slit die data and a 5 kg mixer was used for the capillary propellant. Different solvent levels were required to cause bindup in the two mixers, and the amount of work on the dough would have been different in each case.

3.2 Effect of water level in the processing solvent

The effect of water as a diluent in the processing solvent was similar for both N and NQ propellants which contained Grade F NC and Nigu-Chemie picrite. The effect is illustrated for the N propellant in figure 1. The propellants made with pure acetone had higher shear stresses than the water containing propellants, but this was probably because of the lower total solvent levels used, see Table 2.

The differences between 8% and 14% water were small and had opposite signs in the N and NQ propellants, which indicates that the water content had little effect. The flow curves for N propellants made with 8% and 14% water in the solvent and with Grade C1 NC overlapped, although there was a 5% difference on total solvent content, which indicates that the 14% water solvent propellant would have a higher viscosity if the solvent contents were the same.

3.3 Effect of diluent type in the processing solvent

Both N and NQ propellants were made with ethanol, as well as water, as a diluent for acetone in the processing solvent. The flow behaviour was the same in both propellant types, and is illustrated for the NQ propellant in figure 2. The flow curves of the two ethanol propellants have the same shape, with the lower ethanol content propellant having the higher shear stresses. The flow curves of propellants made with ethanol in the solvent do not show the same degree of sinuosity as the flow curves for propellants made with water in the solvent.

3.4 Effect of picrite type

The effect of picrite type was not the same for the N and NQ propellants. For N propellants in both slit and capillary dies the Bishopton picrite gave a lower slope at low and medium shear rates, and a higher slope at high rates, see figure 3. However, at low and medium rates in the NQ propellant, the Bishopton picrite propellant had a higher slope, and lower stresses. This difference may be due to the differences in viscosity caused by different solvent levels, and this effect will be discussed in Section 4.3.
3.5 Effect of NC type

The effect of changing the NC type was studied in N type propellants made with Nigu-Chemie picrite and solvent water contents of 8% and 14%. The flow curves for the 8% water propellants are given in figure 4. For both water levels the Grade F NC propellants have a lower slope at low shear rates and higher slopes at high rates. The curves for both Grade F NC propellants were always above the curves of the Grade Cl NC propellants. The stresses of the Grade Cl NC propellants decreased more rapidly with decreasing shear rate at low shear rates.

3.6 Effect of temperature

Flow curves determined from slit die measurements of propellants made from Grade F NC and Grade Cl NC and from Nigu-Chemie and Bishopton picrite, are given in figures 5 to 8. Measurements were made at 20°C and 30°C in all cases, and also at 45°C in 2 cases. As expected, the shear stresses decreased with increasing temperature, but the shape of the flow curves also changed. A short plateau region was clearly apparent in the Grade Cl NC, Nigu-Chemie propellant curves at moderate rates, and the plateau moved to higher rates at higher temperatures, see figure 6. Similar, but less distinct, behaviour was apparent for the other propellants. Possible reasons will be discussed in Section 4.3.

The 45°C flow curves have very low values at low rates. During measurement, it was observed that the extrusion pressures at low rates slowly increased with time, but that equilibrium was not reached in the time scale of the experiment. For comparison purposes, it was decided to make the 45°C measurements in the same manner as the lower temperature measurements, and note that the stresses obtained at low rates would probably be underestimated.

3.7 Effect of processing variables on extrudate quality

There was no exact correlation of any processing variable with extrudate quality. However, several general trends were apparent. The extrudates tended to have a matt finish at low shear rates, but the surface tended to become glossy at intermediate rates. The transition to a glossy surface occurred at approximately the same shear rate at which oscillations appeared in the extrusion pressure (see Section 4.3 for more details). At high shear rates the surface often showed slight banding, particularly above 1000 s⁻¹. The Bishopton picrite tended to give a matt finish over a wider range of shear rates than did the Nigu-Chemie picrite.

Use of ethanol instead of water as a diluent gave a glossy finish at low shear rates as well as high rates. Acetone alone as a solvent tended to cause more pronounced banding at high rates.

The die swell of all propellants was very small at all shear rates, and never exceeded 5%.

4. DISCUSSION

4.1 The possibility of slip at the die walls

In a previous study of the rheology of NQ and N type propellants, Baker and Carter (ref.1) reported that the flow curves were often sinuous, particularly at high temperatures. The flow curves had a low slope plateau region at intermediate shear rates, with higher slopes at low and high shear rates. The sinuosity was attributed to effective slip of the dough.
at the die walls ("wall slip") caused by lubrication of the walls by solvent squeezed from the dough.

In cases where wall slip occurs, the effects of the slip must be evaluated before the true rheological parameters of the material can be calculated. The effect of wall slip on the flow curve depends on the die diameter in a manner illustrated schematically in figure 9. The deviation from the "no slip" curve increases with decreasing die diameter. The effect of slip can be determined at any shear rate by measuring the extrusion stresses for dies of several diameters, but with the same length/diameter ratio, and extrapolating the stress vs diameter curve to the stress at infinite diameter. This value corresponds to the no slip stress.

In order to determine the magnitude of the expected wall slip, the capillary measurements in this study were made with dies of widely different diameters, 0.91 mm and 3.27 mm, and two length/diameter ratios, 10:1 and 20:1. It was expected that the flow curves from dies with the same length/diameter ratio, but different diameters, would not overlap and that the degree of mismatch could be used to determine the amount of effective wall slip.

4.2 Evidence for "internal slip" flow

NQ propellant made with 14% water in the processing solvent, GP648, was expected to be one of the most likely to suffer slip because of the high water content in this propellant. Flow curves of GP648 are given in figure 10, and inspection shows that the curves for the different diameters overlap extremely well, and so there is no indication of wall slip in spite of the sinuous shape of the curves. In fact, none of the flow curves produced in this study showed unambiguous evidence of wall slip.

The sinuous shape of the flow curves, with plateaux where the flow curves have very low slope, indicates that some form of slip flow may be occurring. It is proposed here that a type of "internal slip" occurs which is analogous to the internal slip observed in the flow of emulsion and suspension type of PVC.

The flow of unplasticized PVC was studied by Berens and Foulter(ref.3), and also by Nielsen(ref.4). The PVC specimens were cold pressed pellets of fine spheres which were loaded into the rheometer and temperature equilibrated. All flow curves were to some degree sinuous, with a plateau region of minimum slope at intermediate shear rates and increased slope at high and low shear rates. The magnitude of the slope at low rates increased as the temperature increased. In fact, the flow curves showed a striking resemblance to the propellant flow curves in figure 5. Another important observation was that the die swell of the extrudate was very small at shear rates in the plateau region.

The unusual flow behaviour of PVC was explained by postulating the presence of supermolecular flow units which can slip past each other, in a similar manner to the behaviour of rubber particles in raw elastomers which were studied by Mooney(ref.5). Electron micrographs of fracture surfaces of PVC extrudates showed that much of the original particle structure was retained, with the amount of structure depending on the temperature history of the sample. At very low shear rates the material flows by deformation internally in the particles, but as the shear rate increases the particles increasingly slip past each other. At still higher rates the friction between the particles becomes large, and particle deformation again becomes the dominant mechanism for flow. The slipping of the particles, rather than viscoelastic deformation, would explain the low values of die swell observed for PVC in the plateau region.
As already noted, the analogy of the flow behaviour of N and NQ propellants with the behaviour of PVC is very close, and suggests that there may be supermolecular flow units in the propellant doughs. The identity of any such units has not been established, but it is plausible to imagine ungelatinized fibrils sliding past each other, perhaps lubricated by water from the solvent.

Further evidence for an internal slip mechanism is the occurrence of oscillating flow in some dies in the shear rate range at the beginning of the plateau region. The oscillations in stress and flow rate occurred in many propellants in the 3.27 mm diameter dies, and the shear rates at which oscillation occurred are given in Table 3. Note that none of the propellants processed with ethanol as a diluent in the solvent showed oscillating flow, nor did the flow curves have a sinuous shape.

**TABLE 3. EXTRUSION RATES FOR OSCILLATING FLOW IN CAPILLARIES**

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>Ratio</th>
<th>Picrite type</th>
<th>GP No.</th>
<th>Ram Rate (cm/min)</th>
<th>N</th>
<th>NQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>NIGU</td>
<td>659</td>
<td>0(0)′</td>
<td>N</td>
<td>NQ</td>
</tr>
<tr>
<td>A/W</td>
<td>92/8</td>
<td>NIGU</td>
<td>653</td>
<td>0.5-5(na)</td>
<td>652</td>
<td>0.05-0.5(na)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>647</td>
<td>0.5-50(5-50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A/W</td>
<td>BISH</td>
<td>658</td>
<td>0.2-1(na)</td>
<td>651</td>
<td>0.1-1(na)</td>
</tr>
<tr>
<td></td>
<td>A/W</td>
<td>NIGU</td>
<td>655</td>
<td>0(0)</td>
<td>648</td>
<td>0.5(0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>650</td>
<td>0.5-50(2-10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E/A</td>
<td>1/1</td>
<td>NIGU</td>
<td>662</td>
<td>0(0)</td>
<td>660</td>
<td>0(0)</td>
</tr>
<tr>
<td>E/A</td>
<td>1.5/1</td>
<td></td>
<td>-</td>
<td></td>
<td>657</td>
<td>0(0)</td>
</tr>
</tbody>
</table>

Notes:

(1) Data for the 3.27 mm dia x 32 mm die is given first, and data for the 3.27 mm dia x 65 mm die is given in brackets. Zero indicates no oscillation.
(2) na indicates measurement not made.
(3) Threaded die 1.77 mm inside diameter, 22 mm long (see text)

The occurrence of oscillations indicates the presence of some form of slip behaviour, but analysis of the magnitude of the oscillation and the value of the shear rate for onset would be extremely difficult. The main determinants of the magnitude of the oscillations would appear to be the energy storage in deflections of the rheometer and Instron machine, and the flow conditions in the particular die. The interaction of these factors would be different for each different die diameter and length, and would be almost impossible to analyze.

As a further test of whether slip was occurring at the die wall or internally in the propellant, extrusions were made through a threaded die. The die had an internal diameter of 1.77 mm and a length of 22 mm, with a 0.5 mm deep thread cut in the surface. The propellant was GP646, a standard NQ with 8% water in the processing solvent. The flow curves are given in figure 11, and the dotted curve indicates the magnitude of the
pressure oscillations. The flow curves are of apparent shear stress vs apparent shear rate because only one die was used, so the Bagley correction could not be applied to shear stress, and the negative slope of the curves would invalidate the Rabinowitsch correction. The flow curve for the threaded die shows the same type of sinuosity and stress oscillation as curves for other smooth dies, so it is difficult to see how wall slip could explain the shape of the flow curves.

4.3 Effect of internal slip on the interpretation of the effects of processing parameters on flow behaviour

The shape of the flow curves suggests that as the shear rate is increased from low values, the shear stress rises until a critical value of stress is reached. At this stress the internal slip is initiated in the material. As the shear rate increases further, the forces generated between the slipping particles increase, so the slip is able to dissipate a progressively smaller fraction of the input energy. Therefore, at high shear rates the normal molecular flow processes progressively become dominant, and the slope of the flow curve increases to normal values.

The shear rate at which the critical shear stress is reached will depend on the stiffness of the propellant, which is strongly influenced by the solvent level and temperature, as well as the processing parameters under study. The effects of temperature and solvent level can be seen in the flow curves determined from the slit die measurements, figures 5 to 8. Referring to figure 6 it can be seen that the critical shear stress for slip is about 60 kPa. At 20°C the propellant is stiffer, and the critical stress is reached at a lower shear rate than at 30°C. A similar effect of temperature can be seen in flow curves for different temperatures reported by Baker and Carter (ref.1). The critical shear stress is least obvious in the flow curves in figure 8, but the solvent level of this propellant was very high (123%), and so the stiffness of the dough was much lower and the propensity for slip would be much reduced.

The presence of a critical stress for slip greatly complicates the procedures for determining the effects of changes in such variables as picrite and NC types. It is often a practical necessity in processing to adjust the solvent levels to produce acceptable quality doughs when the ingredients are varied, so the effect of the different solvent level may mask the effect of the variable under study. Hence it is not clear at this stage whether the differences noted for changing NC type, picrite type and water content of the solvent related to the variable of interest, or are also affected by the different solvent and processing conditions. However, the differences in flow behaviour caused by changing the type of ingredient are small, and it appears possible to counteract the effect of any variation of one processing parameter by small adjustments to other parameters.

A final comment should be made about the practical effect on extrusion press operation of the very low slope of the flow curves. If the extrusion rate of the press is the controlled parameter, and pressure is allowed to vary, then choosing an extrusion rate near the centre of the low slope plateau region would give an extrudate with low die swell and minimum influence of processing parameters on the flow behaviour. However, if pressure is the controlled parameter, then small changes in pressure could give large changes in flow rate and possibly cause oscillating flow.
5. CONCLUSIONS

Flow curves of shear stress vs shear rate of NQ type propellant doughs had a plateau region of very low slope at moderate shear rates. This plateau was attributed to the presence of an internal slip phenomenon in the dough, which was initiated at a critical shear stress of approximately 60 kPa.

The flow curves had a relatively low slope over the whole shear rate range studied, indicating that relatively small changes in extrusion pressure would produce much larger changes in extrusion rate. Since many factory presses operate in a controlled pressure mode, the pressure would have to be very closely controlled to guarantee a reproducible product. Controlled rate presses would be more suitable for extruding this type of propellant.

The only processing parameters which had a large effect on the rheological behaviour were extrusion temperature and total solvent content. Changes in solvent water content, picrite type and NC type produced relatively small changes in behaviour.

6. ACKNOWLEDGEMENT

The coding of the computer programs used to analyze and manipulate the data in this work was done by Mr D. Kirk.
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APPENDIX I

BAGLEY END CORRECTION FACTORS

The pressure measured by a transducer mounted in the extruder barrel above a capillary die is made up of two components: the pressure arising from viscous flow in the capillary, and the pressure drop in the converging flow in the entrance to the capillary. The flow field at the entrance of the capillary can be quite complex, and the pressure drop is a function of both the extensional viscosity and the elasticity of the extruding material. The flow field within the capillary is assumed to be uniform shear flow, and the pressure drop per unit length of the capillary is proportional to the shear stress at the die wall, the quantity of interest. Since the pressure transducer in the barrel measures the total pressure drop, this value must be corrected for the entrance pressure drop before the true shear stress at the die wall can be calculated.

The most common method of correcting for entrance pressure losses is due to Bagley (ref.6), and the correction factors are often known as Bagley factors. The Bagley method consists in measuring the pressure drop as a function of shear rate for several dies of the same diameter but differing lengths, and assuming that the entrance pressure loss is independent of die length. A plot is made of pressure versus the length/diameter (L/D) ratio for each die for each shear rate, as illustrated in figure 12. The curves for each shear rate are extrapolated to zero pressure, and the intercept on the L/D axis, designated t, corresponds to an extra length of die in which the pressure drop from viscous flow would equal the pressure drop at the die entrance. If a notional die length L', given by

\[ L' = L + \varepsilon D \]  

(I.1)

is substituted in the standard formula for shear stress, equation (I.1), then the true shear stress is given by

\[ \sigma_t = \frac{P \cdot D}{4 L'} = \frac{P \cdot D}{4(L + \varepsilon D)} \]  

(I.2)

where \( \sigma_t \) is the true shear stress, and P is the pressure drop along the die.

An actual Bagley plot for one of the propellants studied is given in figure 12. It can be seen that in this case the value of the Bagley factor at low shear rates is relatively small and constant. However, at high shear rates the apparent Bagley factor increases, but it is believed that this is due to viscous heating in the long die reducing the dough viscosity, and hence pressure, producing an artificially large Bagley factor. It was decided to use a constant Bagley factor for each propellant derived from the low shear rate data, and the values for most propellants were relatively small, being in the range 3 to 6.
APPENDIX II

RABINOWITSCH CORRECTION FOR TRUE SHEAR RATES

The formula for the apparent shear rate was derived on the assumption that the viscosity of the fluid was Newtonian, and that the velocity profile in the die was parabolic. When the viscosity depends on shear rate, as is the case for propellants, the formula for the apparent shear rate must be corrected for the non-parabolic shape of the velocity profile. The correction is known as the Rabinowitsch correction, and is given for capillaries by:

\[ \dot{\gamma}_t = \frac{3n + 1.7}{4n} a \]  

(II.1)

and for slits by:

\[ \dot{\gamma}_t = \frac{2n + 1.7}{3n} a \]  

(II.2)

where \( n = \frac{d(\ln \dot{\gamma}_t)}{d(\ln \dot{\gamma}_a)} \)

This procedure requires taking the derivative of the flow curve. However, since the data consists of a number of discrete points, differentiation of the flow curve would normally be done numerically. In this case any small experimental scatter in the data points would be magnified when finite differences are taken to evaluate the derivative. In the present study the observed flow curve was fitted by a 5th order polynomial using a least-squares procedure, and the derivative was obtained analytically from the fitted curve.
Figure 1. Effect of water content on flow curves of N propellant from capillary dies at 30°C, type F NC, Nigu-Chemie picrite.
--- acetone only, --- 8% water, --- 14% water

Figure 2. Effect of diluent type on flow curves of NQ propellant from capillary dies at 30°C, type F NC, Nigu-Chemie picrite.
--- 8% water, --- ethanol-acetone 1:1,
--- ethanol-acetone 1:1.5
Figure 3. Effect of picrite type on flow curves of N propellant from capillary dies at 30°C, type F NC, 8% water in solvent.

--- Nigu-Chemi, ---- Bishopton

Figure 4. Effect of NC type on flow curves of N propellant from capillary dies at 30°C, Nigu-Chemie picrite, 14% water in solvent.

--- type C1, ---- type F
Figure 5. Effect of temperature on flow curves of N propellant from slit dies, type F NC Nigu-Chemie picrite, 8% water in solvent. Temperatures 20°C, 30°C and 45°C from top to bottom.

Figure 6. Effect of temperature on flow curves of N propellant from slit dies, type CI NC nigu-Chemie picrite, 8% water in solvent. Temperatures 20°C and 30°C from top to bottom.
Figure 7. Effect of temperature on flow curves of N propellant from slit dies, type F NC Bishopton picrite, 8% water in solvent. Temperatures 20°C and 30°C from top to bottom.

Figure 8. Effect of temperature on flow curves of N propellant from slit dies, type C1 NC Bishopton picrite, 8% water in solvent. Temperatures 20°C, 30°C and 45°C from top to bottom.
Figure 9. Schematic representation of the effect on flow curves of slip at the die walls.

Figure 10. Flow curves of apparent shear stress vs apparent shear rate of NQ propellant from capillary dies at 30°C, type F NC, Nigu-Chemie picrite, 14% water in solvent.
Figure 11. Flow curves of apparent shear stress vs apparent shear rate of NQ propellant from threaded die at 30°C, type F NC, Nigu-Chemie picrite, 8% water in solvent. ——— lower value of stress oscillation.

Figure 12. Bagley plot of total pressure drop across die vs length/diameter ratio of die. Diameter 0.91 mm, lengths 8.9 mm and 17.6 mm.
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**THE EFFECT OF PROCESSING VARIABLES ON THE "INTERNAL SLIP FLOW" OF A TRIPLE BASE GUN PROPELLANT DOUGH**

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The rheological behaviour of triple base gun propellant doughs of N and NQ types was measured with an extrusion rheometer at temperatures of 20°C, 30°C and 45°C, using slit and capillary dies. The propellant doughs were made from two grades of nitrocellulose, and from picrite obtained from two sources. Acetone/water mixtures and acetone/ethonal mixtures were used as processing solvents. Most of the processing variables had little effect on flow behaviour. It was found that a type of internal slip occurred in the dough at a shear stress of about 60 kPa, and this had a significant effect on flow behaviour.