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# Sample geometry as critical factor for stability research

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**Abstract**

Stability research on gun propellants has been widely performed by microcalorimetry since the 1980s. TNO Prins Maurits Laboratory has already a broad experience since the early 1970s. In the past many studies were performed, to investigate the influence of oxygen, humidity etc. Less attention was paid to two other important aspects, namely the sample geometry and the filling degree during the microcalorimetric test.

A statement in the old Dutch military literature presents the following “It is a well-known fact that the free surface influences the decomposition rate of the gun powder, i.e. unground propellant decomposes slowly in comparison to ground propellant”. This is the same for all types of propellant (Amsterdam, February 1924), which implies research on this topic, related to the stability prediction measured by microcalorimetry is important.

Since the decomposition of nitrocellulose is influenced by the amount of oxygen and the surface area, the best way to investigate the stability of gun propellants is to measure it ‘ammunition like’. This means that a combination of the propellant grain size and the filling degree of the ammunition should be used for investigation. For small caliber ammunition the filling degree is close to 95%, and for large caliber bag ammunition (e.g. 155 mm) it is around 60%. As a result on these important aspects, TNO has developed five different sizes of sample vessels, to investigate the propellant grains in the most ‘ammunition like’ condition.

In this paper, an overview is given of the influences of relative humidity, different grain sizes and available oxygen. The available oxygen is adjusted by changing the oxygen content of the air or by changing the filling degree.


*Keywords:* Microcalorimetry; Filling degree; Grinding; Propellants; Stability; Heat flow

## 1. Introduction

Propellants are notorious because of their intrinsic instability. Where in history the disasters led to storage outside inhabited areas (powder explosions in Delft (NL), 1654), nowadays accidents with solid propellants lead to an increase in research. The first efforts in the development of guncotton were studded with disasters. In 1847, an explosion in the first year of operation destroyed the first factory for the manufacture of guncotton at Faversham (UK) [1].

In the earlier years, surveillance was based on the 65.5 °C red fume-test. This method indicates the stability of propellant in a closed glass bottle, which contains the propellant grains in their original form. The drawback of this methodology was and still is the interpretation of the results by the human eye. An improvement in stability-research techniques resulted from the introduction of the HPLC method.

Comparing the different STANAGS related to stability research by HPLC (4117, 4527, 4541 and 4542), the propellant is aged in its original sample geometry,

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except for stick propellants, which have to be cut into smaller lengths according to these STANAGS. The filling degree (∼ 30%) is low, which is still on the safe side. After the ageing period the grains are ground into particles of less than 2 mm to facilitate extraction of the stabiliser. The HPLC-methods only give information on the expected stabilizer depletion for 5 or 10 years.

In all well-known literature it is concluded that the decomposition of propellants generates a temperature increase inside the propellant caused by the decomposition energy. This is a result of the sum of all chemical processes which occur during the ageing (and storage) of the gun propellant, directly resulting in a decrease in calorific value (heat generation) and possibly a run-away reaction.

After extensive research [2–7] on the ageing process of nitrocellulose (NC) based gun propellants, surveillance in The Netherlands is based on the heat generation. Since the beginning of the 1970s the heat generation in an accelerated ageing process has been carried out using the heat flow calorimeter (TNO-HFC). The heat generation is measured for an unground sample during 1 week at 85 °C (358 K). The result is used to calculate two parameters. The first parameter to be determined is the safe diameter [8–10] of the storage geometry, a parameter which is characteristic for the self-ignition hazard. The second parameter is the expected decrease in calorific value for judging the changes to the performance [11]. Both the safe diameter and the decrease of calorific value are being established for a future storage period of 10 years.

Usually, surveillance of NC-based propellants is performed without considering the environmental conditions of the stored propellant, except for the storage temperature. Effects of other influences like relative humidity (RH), amount of oxygen (filling degree of the test-vessel) and the particle size (ground/unground) are quite often discussed in the literature, but not yet adopted for test procedures [12–15].

The ambient RH will vary with location and time, from season to season or from day to day in coastal areas, making incorporation in a standard test procedure complicated. STANAG 2895 [16] has covered most of the external effects. An overlooked aspect is, for instance, that propellants for surveillance purposes can be stored in a magazine different from the magazines containing the munition articles. This is often the case in The Netherlands.

Another factor that influences the chemical stability is the available oxygen. In some investigations the stoppers of glass tubes containing the ageing propellant are lifted regularly to keep the oxygen content at a more or less constant level. The effects of the oxygen content as well as the effects of grinding will be discussed in this paper.

## 2. Equipment

The HFC used for these investigations at TNO-PML is of the van Geel type [17]. It consists of an aluminium block, which acts as a large heat sink to keep the temperature constant. A Peltier element in good thermal contact with the bottom of a stainless steel vessel, measures the heat generated by the sample in the passive mode. The volume of the standard vessel is 70 $cm^3$ but other sizes for performing HFC experiments are available.

The HFC technique, with a relative large measuring vessel (availible sample sizes, see Fig. 1), has the great advantage that the propellant can be used in its original form (no cutting or other pre-treatments), and

Fig. 1. Available sample vessels for propellant stability research.

in the condition as-ammunition-like, with respect to the loading density.

The temperature to perform measurements has a range from 50 to 200 °C, which gives the possibility for shorter ageing periods. Other stability determination techniques such as DSC or DTA are never used in The Netherlands for surveillance of gun propellants, because the propellants are inhomogeneous and these techniques use very small sample quantities.

## 3. Background

### 3.1. Safe diameter

*Definition*: Maximum diameter of a cylindrical filled container of propellant for which self-ignition is just excluded.

When a propellant is stored, no self-ignition will occur as long as equilibrium exists between heat generation and heat transfer to the surroundings. Whether this equilibrium will establish depends among others on the storage temperature. Another factor is the resistance encountered by the heat flow on its way into surroundings. This resistance depends on the thermal conductivity of the propellant and the dimensions of the propellants mass (package size). At a certain diameter the heat transfer will lag behind and the temperature will continue to rise, resulting in self-ignition (Fig. 2).

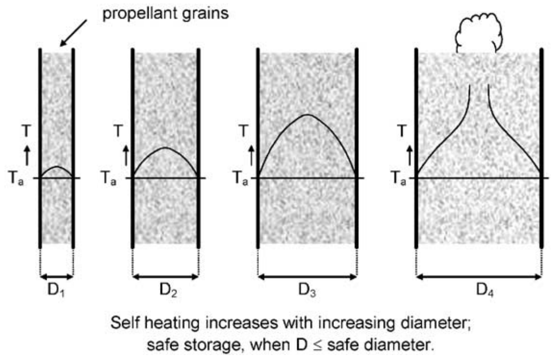


Fig. 2. Schematic overview of the meaning of the safe diameter.

Also the ageing of the propellant plays a role, because the heat generation depends on the presence of stabilizer derivatives. Based on this consideration the self-ignition hazard, for each storage temperature, may be characterized by calculating the safe diameter [10]. The definition is also valid for other sample geometry.

For the calculation of the safe diameter it is assumed, that during the considered storage period of 10 years the propellant will be exposed to extreme storage conditions for 2 weeks, the storage conditions being ambient temperature in the magazine during the rest of the period. The extreme storage conditions used for the calculations are a daily temperature profile of 9 h at 35 °C; 5 h at 40 °C; 5 h at 60 °C and 5 h at 71 °C.

According to Merzhanov [18] and Barendregt [19], the formula to calculate the safe diameter, $D_{\mathrm{Ta}}$ (m), at an ambient temperature, $T_a$ (K), is as follows:

$$D_{T_a} = \frac{2.7\,\lambda}{2} + \sqrt{\frac{(2.7\,\lambda)^2}{4} + \frac{4RT_a^2\delta_c\lambda\exp(E_a/R(1/T_a - 1/T_m))}{\rho_b E_a Q_{max}}}$$

The following parameters are used [9].

$E_a$, activation energy (J mol$^{-1}$); $R$, gas constant (J mol$^{-1}$ K$^{-1}$); $T_a$, ambient temperature (K); $T_m$, measured temperature (K); $\delta_c$, shape factor (−); $\lambda$, thermal conductivity (W m$^{-1}$ K$^{-1}$); $\rho_b$, bulk density (kg m$^{-3}$); $Q_{max}$, maximum heat generation (W kg$^{-1}$).

Based on the highest temperature considered in the 2 weeks extreme storage, 71 °C (344 K) is used for the ambient temperature. The thermal conductivity and bulk density depends on each propellant lot.

### 3.2. Ballistic stability

Based on theory and confirmed with closed vessel tests, a proportional relation exists between the decrease of calorific value of the propellant ($Q$ (J)) and a decrease in muzzle velocity ($V_0$ (m s$^{-1}$)). In formula $V_0 = a$Q [11], where it has been experimentally found that the factor $a$ varies between 0.1 and 2 (J s m$^{-1}$). A decrease in calorific value of the propellant during the storage period is a result of the exothermal decomposition of the propellant. This decrease is equal to the total quantity of heat generated during the storage period. During the accelerated ageing in the HFC, the heat generation is measured.

It can be concluded from the above-mentioned that the decrease in muzzle velocity after 10 years of storage in The Netherlands is very small (<1%). And even after 10 years of storage in the tropics it will be in the order of a few percent. The acceptable decrease depends on the actual application of the propellant.

### 3.3. Surveillance process

The surveillance process in The Netherlands is split-off in two parts, namely the acceptance of new propellants and the surveillance of old propellant lots. During the acceptance and surveillance control the safe diameter of the propellant is determined for a temperature of the surroundings of 71 °C (344 K). In accordance with NATO requirements such a temperature must be reckoned with. It should be remarked in this connection that it has been established experimentally that the temperature of a propellant container can really run up to as high as 344 K when exposed to direct radiation of sunlight.

## 4. Results

### 4.1. Influence of humidity

It can be expected that relative humidity (RH) will have an influence on the chemical stability of NC based propellants. During decomposition of propellants, $NO_x$ is released which reacts with water to form nitric acid. Nitric acid is considered [20] to react with the hydrolysed propellant giving nitrous acid, which catalyses the decomposition reaction of NC based propellants. In general, for single base (SB), double base (DB) and rocket propellants, it holds that the higher the relative humidity the larger the heat generation rate. The moisture content of the propellant also influences the heat production.

In the surveillance procedure a sample preconditioning is not yet performed as a standard. The samples are aged in vessels or glass tubes under closed "atmospheric conditions" (e.g. STANAG 4117).

It is evident from the HFC data that the RH conditions change the heat production of all considered types of propellants. At 85 °C, the heat production at highest RH(s) is about 2–3 times the heat production at the lowest RH (Fig. 3). The data indicate that this increased heat production is due to an acceleration of the decomposition as the RH increases.

### 4.2. Influence of amount of oxygen

Another factor that influences the chemical stability is oxygen. The presence of excess oxygen is reported to increase the heat production of the

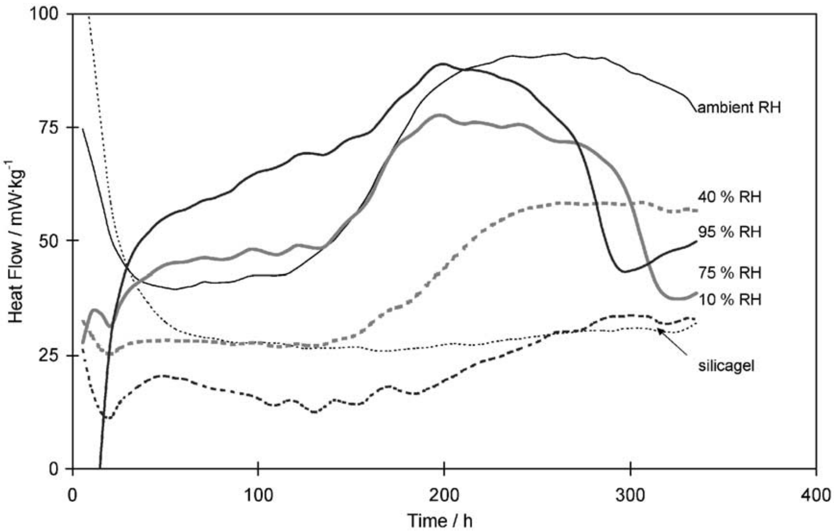


Fig. 3. Heat generation as function of relative humidity for DB propellant KB 6937 at 85 °C. In one experiment silicagel is added to the sample vessel in order to reduce the relative humidity. The ambient RH in The Netherlands is usually assumed to be about 60–70%.

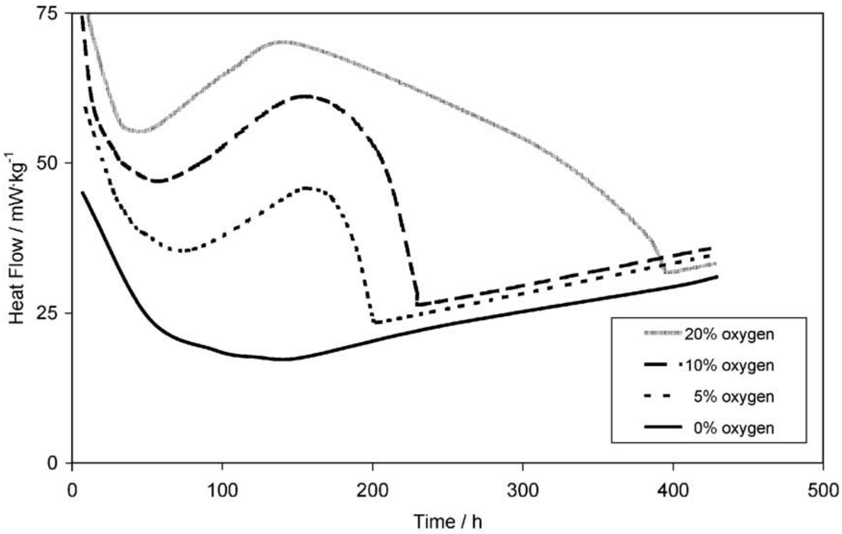


Fig. 4. Heat generation in smokeless powder at 85 °C with variable oxygen concentration.

propellant as NO can be oxidized to $NO_2$ which catalyses the decomposition of the propellant [20]. In some investigations the stoppers of glass tubes containing the ageing propellant are lifted regularly to keep the oxygen content at a more or less constant level and provide a kind of worst case scenario. In practice the available oxygen depends on the filling degree and the air-tightness of the packaging.

In Fig. 4 an overview of the relation between the amount of oxygen in the vessel and the heat generation is given [21].

Indirectly the filling degree of the test vessel determines the amount of free oxygen. In case of a completely filled sample vessel, the amount of oxygen available for the oxidation reaction is small, compared with the amount of reaction surfaces. This will lead to a lower heat generation. In Fig. 5, the effect of the filling

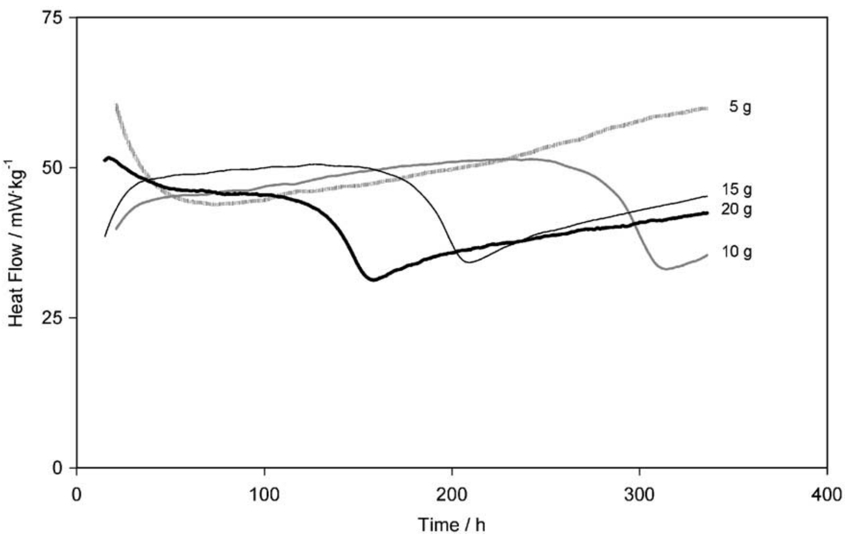


Fig. 5. Heat generation as function of filling degree for DB propellant KB 7306 at 85 °C.

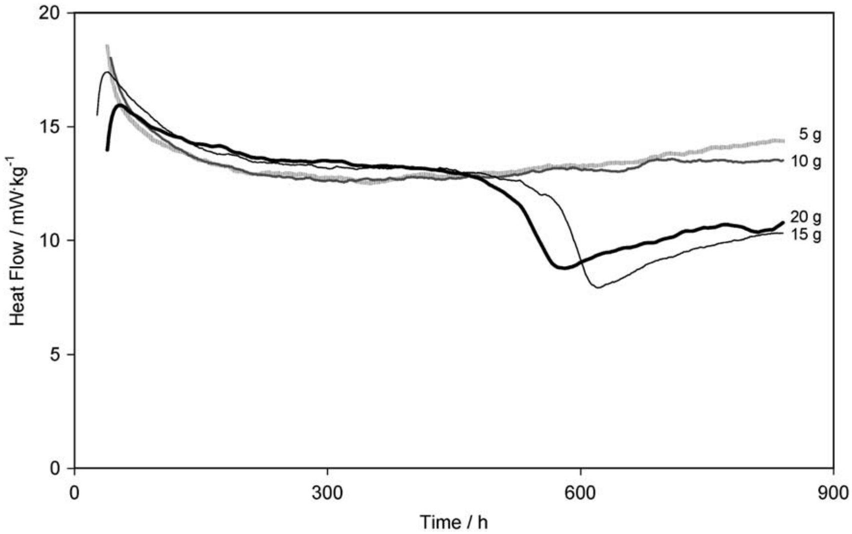


Fig. 6. Heat generation as function of filling degree for DB propellant KB 7306 at 75 °C.

degree is presented for a DB propellant stabilised with 3% ethyl centralite (EC) in a 70 $cm^3$ vessel.

Figs. 4 and 5 also show that the heat generation drops to a lower level after oxygen depletion. As might be expected, the effect of the filling degree is observed at lower temperature (e.g. 75 °C, Fig. 6) and also for SB propellants at 85 °C (Fig. 7).

For the SB propellant, the loading density is 0.071 g $cm^{-3}$ for the 5 g sample and 0.285 g $cm^{-3}$ for the 20 g sample. The original ammunition article has a loading density of 0.292 g $cm^{-3}$.

In an earlier version of STANAG 4582, a preconditioning at a relative humidity of 69% was suggested. To determine the effect of the relative humidity in combination with the loading density, KB 7071 was investigated after preconditioning at 69% RH. Fig. 8 shows that the reactions are influenced by the higher relative humidity. The resulting heat productions

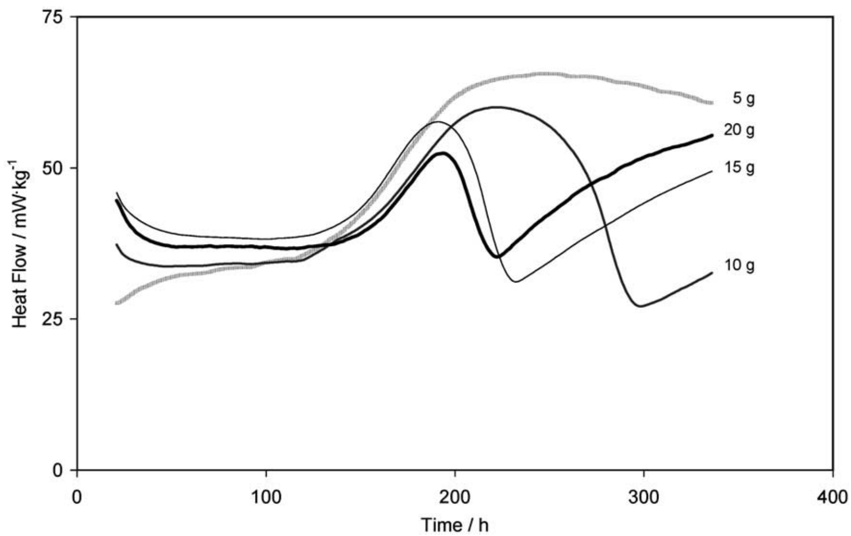


Fig. 7. Heat generation as function of filling degree for SB propellant KB 7071 at 85 °C and ambient RH, in a 70 $cm^3$ sample vessel.

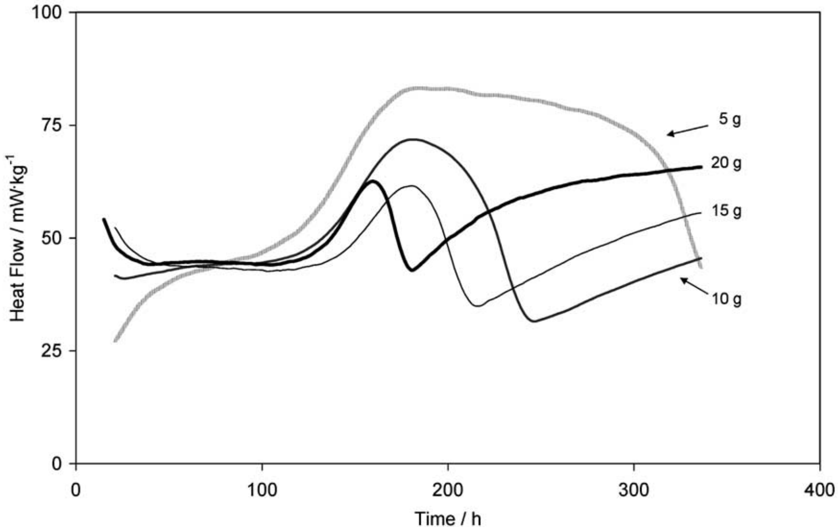


Fig. 8. Heat generation as function of filling degree for SB propellant KB 7071 at 85 °C.

are in the same range; only the reaction takes place earlier.

Sample vessel was closed after 24 h preconditioning at a relative humidity of 69%.

### 4.3. Influence of surface area

During the experimental program it was observed that for some propellants the heat generation was relatively high during the first few hours of the experiment. This high heat flow effect was not observed for triple base (TB) propellants [3]. The nitroguanidine (NQ)-group has a stabilizing effect resulting in hardly any red fumes in the 65.5 °C test. The influence of the surface area of propellant grains has been investigated with HFC experiments on a SB propellant containing 83% NC and 1% diphenylamine (DPA) and DB propellant containing 55% NC, 41% nitroglycerine

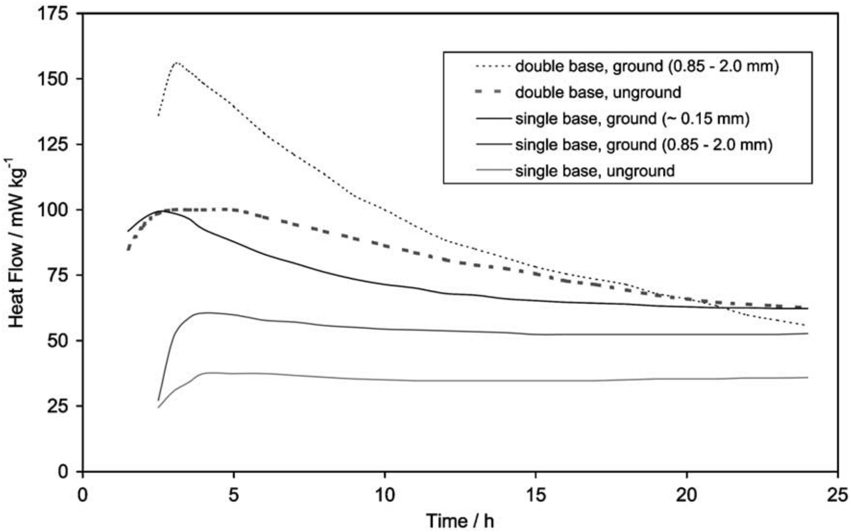


Fig. 9. HFC measurements with the different initial effects caused by particle size.

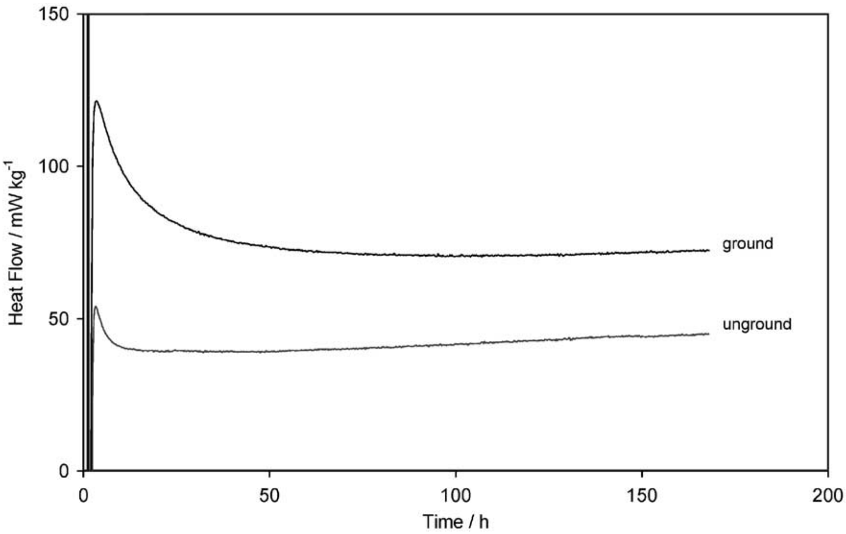


Fig. 10. HFC measurement on double base propellant KB 7306 (tubes with a diameter of 5.3 mm), showing the effect of pretreatment (ground to a size of about 2 mm).

(NG) and 1.7% stabilizer (EC, methylcentralite (MC) and akardite II (AKII)). Besides experiments with unground propellant grains, experiments were carried out with ground samples of varying particle sizes of around 1 and 0.15 mm on the average.

From the curves shown in Fig. 9 it can be concluded that the surface area of the propellant affects the initial heat flow. The initial heat flow of unground propellant is small, while for propellants that had been ground to around 0.15 mm the initial heat flow is increased by a factor of two.

The results suggest that the grinding operation allows oxygen to react rapidly with the propellant. This effect was only observed for single and double base

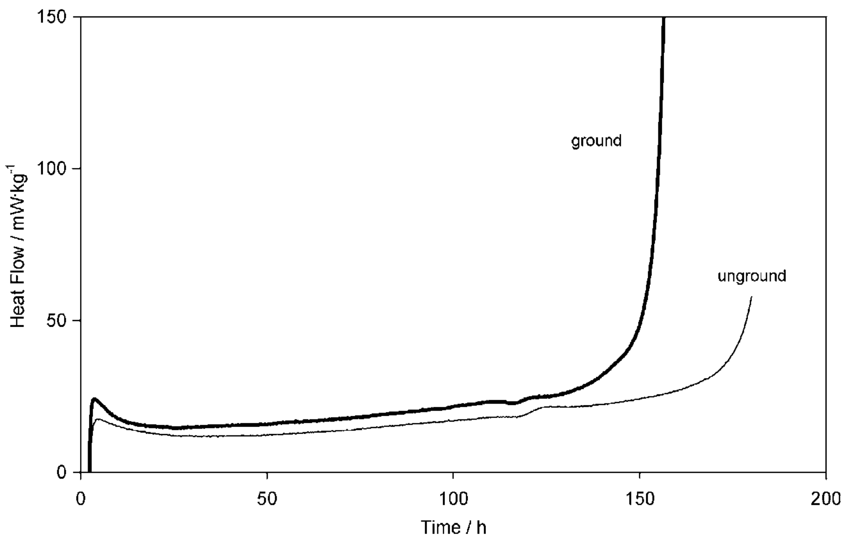


Fig. 11. HFC measurement on triple base propellant KB 7304 with the effect of pretreatment.

propellants. Investigations on several triple base propellants did not show this effect.

### 4.4. Influence of particle size

Surface area also has a strong influence on the whole heat generation curve. This effect is observed in the measurements and presented in Fig. 10 for a double base propellant.

In Fig. 10, a propellant consisting of 54% NC, 26% NG and 3.1% EC is investigated. A higher initial heat flow was observed along with a heat generation that was a factor of two higher for the ground sample. Sample size will affect the calculated safe diameter (parameter from TNO calculations) or the acceptance level (according STANAG 4582). For both a conservative value will result.

In Fig. 11 the heat flow from a ground and unground sample of a propellant with the composition 30% NC, 21% NG, 49% NQ and 0.4% *m*-nitro-aniline (MNA) are compared. The difference in initial heat flow is small, probably caused by the presence of nitroguanidine [3], but the curve shows a run-away which is approximately 40 h earlier for the ground sample. In practice it means that the expected lifetime of the ground sample is 2–3 years shorter. A shorter service life has economic (replacement of ammunition) and environmental consequences (decommissioning of the ammunition).

## 5. Conclusions

- The amount of available oxygen influences the reaction rate and as a result, the heat generation. So a ‘not ammunition like’ filling degree implies incorrect predictions for the safe lifetime.
- Increasing relative humidity will lead to an increase in the heat generation. So, it is preferred that the relative humidity is representative for the storage conditions.
- It was observed that for some propellants, independent of temperature, the heat generation was relatively high during the first days of the measurement. This initial effect was not observed in triple base propellants, probably caused by the stabilizing effect of nitroguanidine.
- Based on the results of the HFC measurements grinding the propellant sample results in curves that have the same shape, but are shifted with respect to heat generation or with respect to time to runaway, mostly leading to a too conservative safe diameter and decrease in calorific value.
- In case the propellant grains will not fit the sample vessel, the best way is to adapt the vessel. If this is impossible, try to minimize the grinding activities.
- In this connection it is advisable to carry out the heat flow calorimetry test with unground propellant grains in the condition, as the propellant grains are stored, so “ammunition like”. The TNO-HFC is designed to facilitate these measurements to a large extent.

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