



Testing Propellants by Calorimetry

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Fig 1. The French battleship “Liberté” destroyed by a propellant explosion in 1911.

The need to survey the stability and compatibility of explosives in general and propellants in particular is beyond discussion.

During the more than 100 years that nitrocellulose has been in use as a propellant, an enormous number of tests have been devised to survey its stability. The majority of these tests are rather simple and empirical in nature. During the last decade or so, however, modern analytical methods have been introduced in the explosives field, and are often used in parallel with older methods. Modern methods give real information about the components studied, but the translation of the result into terms of stability, compatibility and remaining stable life of the complex mixture of ingredients in a propellant is no easy task.

Propellants are among the least stable and most difficult explosives to analyse. The main component of propellants is the polymer is nitrocellulose, or, more precisely a deliberate mixture of nitrocelluloses with varying molecular weights and varying of degrees esterification. To determine the molecular weight distribution and also the degree of esterification of the different fractions is of course possible with modern methods. But to carry out such determinations with the high precision needed to detect the small changes associated with a dangerous deterioration of the propellant is a highly demanding task. To turn the determinations into simple routine tests is not possible today. This has led to the

development of indirect tests of stability instead, such as the determination of stabilizer changes. While stabilizer changes are connected with the nitrocellulose degradation, not all reactions involved in the nitrocellulose decomposition affect the stabilizer. Furthermore the reactions involved are numerous and not fully established.

A way out of these difficulties is to measure the total reaction heat evolved by the different simultaneous and consecutive reactions in the propellant. This idea is not new, though it is not until now that it has become interesting due to the development of very sensitive calorimeters.

Already in 1883 Hess¹ in Germany proposed the study of heats of reaction for the estimation of the stability of explosives, but his equipment (Figure 2) was too crude, and used sample sizes of up to 100 g. Hess's technique was never used to any great extent. The English silvered vessel test is a later adoption of the same principle. In Germany, Siebert took up the method about 50 years after Hess and then inspired a coworker, Frey², to develop a microcalorimeter with specially designed sample holders. Van Geel³ in Holland has also designed a calorimeter particularly for stability studies. The French Calvet calorimeter^{4, 5}, while constructed for general studies, has also been used for some years for the study of propellants and explosives.

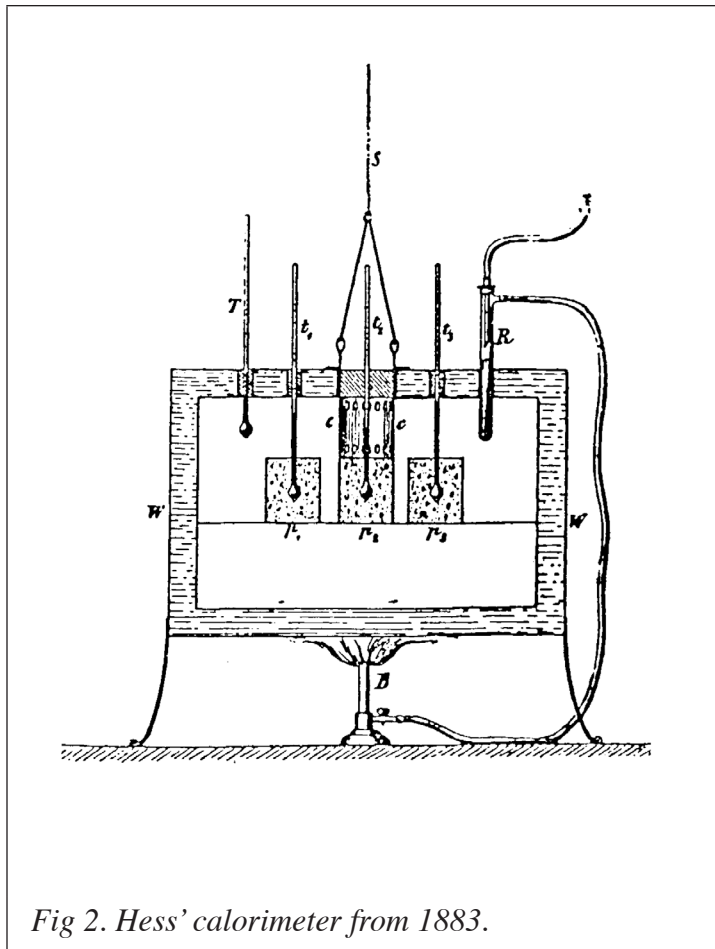


Fig 2. Hess' calorimeter from 1883.

The three last-mentioned calorimeters normally use 25—50 g samples and are mono-calorimeters, i.e. are designed for only one sample at a time. With the LKB 2277 calorimeter⁶ used here the sample size can be kept down to 1 g, and four samples can be run at the same time, the latter being interesting for comparative tests. Even four parallel runs is a small number when testing propellants since the decomposition reactions are slow and therefore require long testing times. This necessitates intermittent measurements and storage of the propellants in an oven between runs. Such a procedure is of course much easier if the sample size is small reducing any danger of explosion or evolution of hazardous amounts of nitrogen oxides. Furthermore the LKB calorimeter attains equilibrium within 1 hr or less making it possible to measure initial reactions.

EXPERIMENTAL

Instrument

LKB 2277 Microcalorimetry System with four measuring cylinders. Thermostat bath temperature constancy: $\pm 2 \times 10^{-4} \text{C}$, according to specification. Measuring precision: $\pm 2 \%$ at the highest sensitivity, corresponding to a full scale deviation of $3 \mu\text{W}$, also accord-

ing to specification.

Glass ampoules and stainless steel ampoules with an effective volume of 3 and 5 ml respectively were used. The glass ampoules were sealed with an aluminium cap and rubber and teflon packing. To confirm the tightness of the ampoules they were weighed before and after the runs. Both sample and reference ampoules show a certain weight decrease. The caps of the glass ampoule evidently give a weight loss of a little less than 3 mg that occurs quickly. In addition the sample ampoules give a weight loss through gas leakage of about $50 \mu\text{g/day/g}$ sample with the propellant used in the runs described here. A leakage of this order does not affect the measurements.

To minimize disturbances the ampoules were introduced into the measuring cylinders by lowering them stepwise over a period of 30 mins. It is probably possible to shorten this time without any disadvantage.

Propellant

A double-base propellant with the following composition was used:

Nitrocellulose (13.1 %N)	59.6%
Diethyleneglycol dinitrate	39.0%
Ethylcentralite	1.3%
Graphite	0.1%

Reference substance

Fine glass beads dried over silica gel were used as a reference substance in order to give both sample and reference ampoules the same heat capacity. Precise agreement does not seem necessary.

RESULTS

Runs have been made in the range 60°C to 80°C at 5° intervals and with samples from 0.5 to 2.2 g. The registered power output is proportional to the mass of the propellant (see Figure 3).

Figure 4 shows the long-time behaviour of the propellant at 80°C . After an initial, relatively constant phase lasting about one day the heat output decreases to a minimum. There follows a slow increase of about $50\text{--}100 \text{ nW/g}$ propellant/day. In the case illustrated here the power output had risen to $16.5 \mu\text{W/g}$ after somewhat more than 90000 mins.

Humidity has naturally a great influence on the degradation of nitrate esters and there-

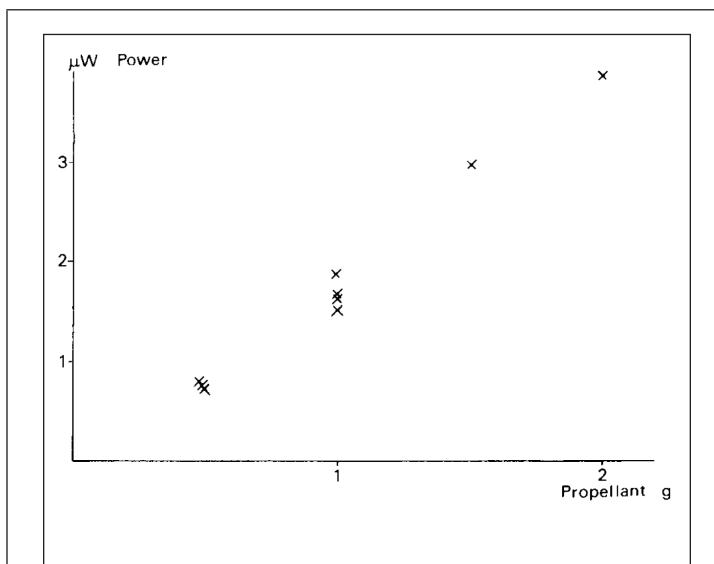


Fig 3. Dependence of heat output on sample weight.

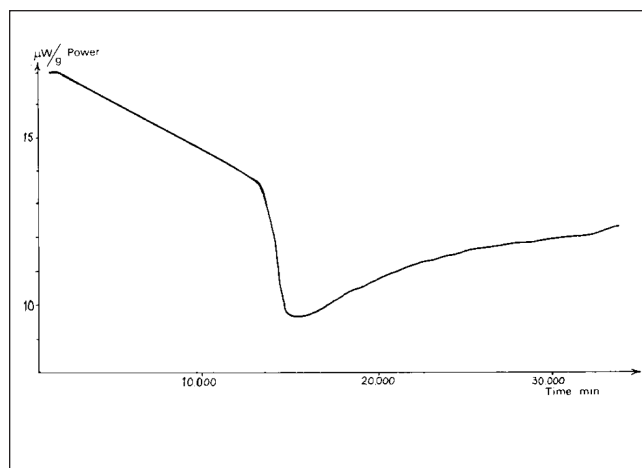


Fig 4. Long-time run at 80°C .

fore of propellants. Some runs were made with propellants that had been moistened at 52 % and 100 % RH and with samples dried in an desiccator over silica gel. These treatments cannot be expected to have changed the propellant grains homogeneously, but they affect the initial decomposition stages markedly. Higher humidity gives a higher power output and an earlier occurrence of the minimum. The dried sample shows an accelerating power output during the first two days. All the samples tend to reach the same value as the more or less surface-located changes caused by the preliminary treatments are smoothed out.

Figure 6 Finally, shows an Arrhenius' plot of runs at five different temperatures between 60 and 80°C, from which an activation energy of about 26 kcal/mole can be calculated.

DISCUSSION

The evaluation of the calorimeter measurements depends on the problem they are used for. The simplest case is compatibility studies, not exemplified here, when the behaviour of a mixture can be referred to that of the simple components as standards.

When calorimetry is applied to the study of propellant stability, the ideal case is that concerning a propellant that has been studied a short time after its manufacture and its degradation followed until the end of the induction period. This renders an easy estimation of the remaining stable life possible at later occasions.

With no such initial measurements available, the case becomes more complex. Frey² integrates the effect until the end of the induction period, assuming a constant decomposition velocity. From measurements at different temperatures and by extrapolating the over-all reaction velocity to the storage temperature, one can estimate the remaining stable lifetime of the propellant.

Van Geel³ uses a more complicated approach, which requires a great number of mea-

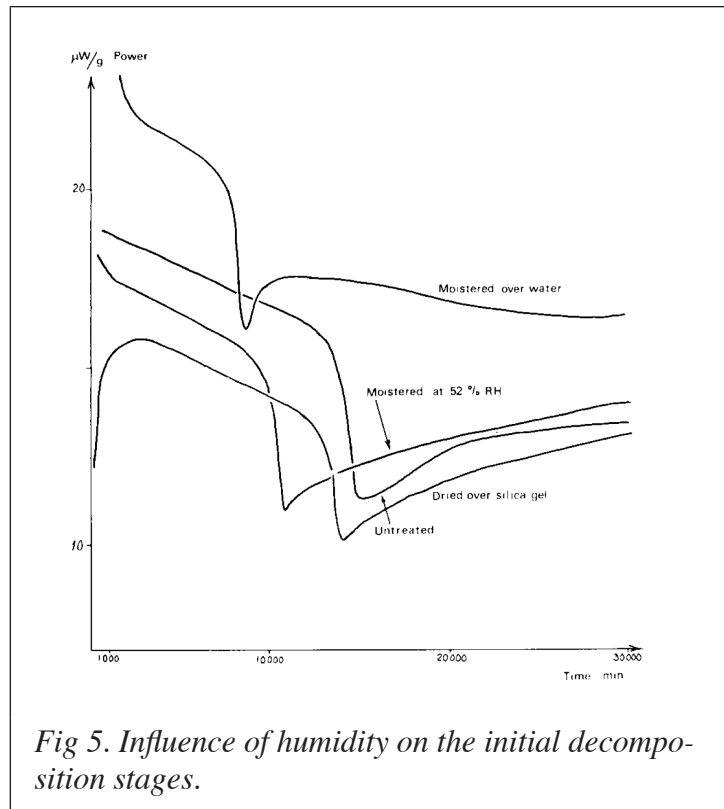


Fig 5. Influence of humidity on the initial decomposition stages.

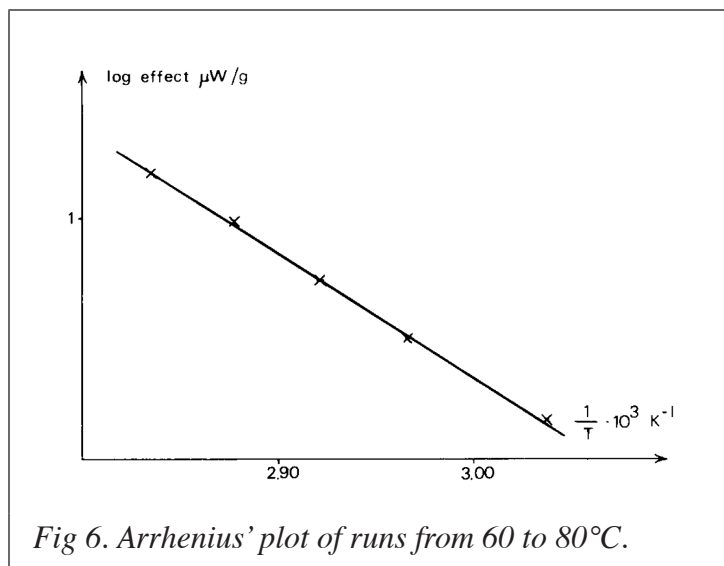


Fig 6. Arrhenius' plot of runs from 60 to 80°C.

surements. From runs at different temperatures and the proposition

$$q = \frac{dQ}{dt}$$

where q is the power, and Q the total heat evolved by the propellant until time t , he derives activation energies, which he uses to calculate critical values according to Frank-Kamenetskii's thermal explosion theory.

The application of thermal explosion theory is, of course, of great interest and the theory in its simplest forms has been referred to widely. The practical cases, however, present some difficulties not taken into account by the simple Semenov and Frank-Kamenetskii theories, as the explosives or propellants are usually parts of irregular ammunition items and are always packed in boxes and are surrounded by different kinds of more or less heat insulating wrappings. An initial attempt to handle such problems has been made by Boddington, Griffiths, Scott and Hansson⁷ and shows an important influence of packing materials on critical sizes, which should be taken into account when dealing with surveillance problems.

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