Ampoule Microcalorimetry for Stability and Compatibility Testing of Explosives and Materials

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ABSTRACT

Microcalorimetry is a powerful tool for solving compatibility and stability problems for explosives and other materials. It is a very general method due to the fact that practically all physical and chemical processes are accompanied by heat exchange. The high sensitivity of the method makes it possible to carry out measurements at temperatures close to real conditions and to detect very slow (ageing) reactions. In compatibility studies, the heat flow is measured separately for the two materials and for a mixture of these. The experimental heat flow curve for the mixture is compared with a calculated hypothetical curve for the same mixture with no physical and chemical interactions. An interaction energy is defined as the time integral of the difference between these curves. Heat flow data, interaction energies and physical and chemical properties of the materials are considered in the interpretations. Three different compatibility problems are discussed.

Microcalorimetry yields information about the stability of propellants and high explosives. The heat flow is a measure of the decomposition rate.The difference in stability of a stabilized propellant and the same propellant without stabilizer is demonstrated. It is shown that the lowest decomposition rate that could be detected occurs at a temperature that corresponds to an autocatalysis time of approximately 25 years. Furthermore, microcalorimetry could be used for stability testing of pyrotechnics. An example concerning the oxidation of boron in a pyrotechnic igniting composition is presented. Quantitative considerations show that this oxidation process may become an important ageing effect after long time storage in open air.

INTRODUCTION

Compatibility

High explosives, propellants and pyrotechnics for ammunitions, missiles and similar products are usually exposed to a variety of other materials, e.g. plastics, adhesives, sealants and metals, either by direct contact or via the atmosphere within the product. It is of vital importance that all materials are compatible, i.e. that they do not interact chemically or physically with each other in the product under consideration. Such interactions may give rise to misfunction or safety hazards in handling or reduced shelf life. There is usually a large number of possible material com¬binations, and consequently a multiplicity of different types of possible interactions with a wide range of reaction rates. A suitable analysis technique for com¬patibility studies must therefore be very “general” and also very sensitive. In this paper we show that microcalorimetry is a powerful technique that meets these requirements. The generality of the method follows from the fact that practically all physical and chemical processes are accompanied by heat exchange.

The high sensitivity of microcalorimetry to these reactions offers some important advantages compared to standard compatibility testing methods like vacuum stability test (1), DTA (2) and weight loss tests (3):

1. Measurements can be carried out at lower temperatures than used in standard methods. Transformation of the results to normal temperature conditions will thus be more realiable.

2. It is possible to detect even very slow reactions. “Long-term” incompatibility, i.e. interactions of very low rate between materials, that affect safety or functions of a product after several years of storage, may thus be predicted.

Stability

Microcalorimetry is also a suitable method for stability studies of explosives (4, 5) where the heat produced in the decomposition of the materials is measured. Again, the high sensivity of the microcalorime-ter makes it possible to use lower measuring temperatures than employed in e.g. the vacuum stability test. Rate constants, activation energies and other kinetic parameters could thus be obtained for temperatures very close to real conditions.

In order to illustrate the versatility of microcalorimetry in the field of explosives, we present results for a number of stability and compatibility problems representing different physical and chemical conditions. All examples are chosen from routine investigations of explosives and materials.

EXPERIMENTAL

A prototype of a LKB Multi-channel Microcalorimetry System 2277-020 equipped with four ampoule calorimeters 2277-201 was used in this work. All measurements were made at 70°C. The instrument was connected to a minicomputer (ABC 80) in order to facilitate data collection, evaluation and curve plotting. The computer software was developed at AB Bofors, Karlskoga, Sweden.

All materials were used as received, unless otherwise specified. Approximately 1 gram of the samples were packed in 2.5 ml glass ampoules, which were sealed with a glass disc and a UV-curing adhesive (Loctite 358). This sealing technique yields a very tight ampoule with a minimum of polymeric sealant present. 1.5 grams of high purity sea sand was used as the reference sample.

Heat flow data were recorded either continuously or as “single point” measurements. In the former case, the samples were kept in the calorimeter throughout the experiment, and the heat flow was recorded by the computer at fixed time intervals. The “single point” technique was applied to experiments of long duration. In this method, the ampoules were stored in an oven at 70 °C between each measurement point.

All results have been normalized to unit sample weight.

RESULTS AND DISCUSSION

Compatibility studies

Anaerobic adhesives and sealants are frequently used in ammunition, missiles and similar products. These materials contain reactive peroxides and acrylic esters, which could interact with various explosives. A compatibility study of the system Loctite 270/single base propellant (16/84 wt%) is shown in fig. 1.

Curve A represents the heat flow of the propellant alone. Its slightly exothermic behaviour is discussed in detail in a subsequent example. The pure (uncured) Loctite 270,

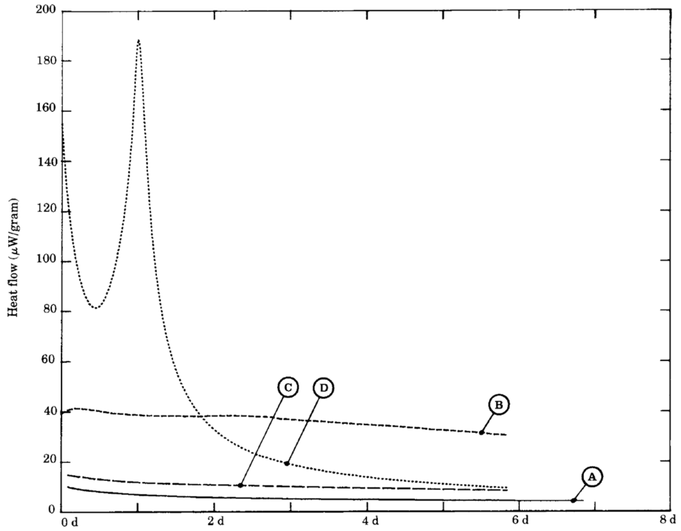

Fig. 1. Calorimetric curves for the system Loctite 2701 single base propellant. (A) propellant, (B) uncured Loctite 270, (C) and (D) "non-interaction" and experimental curves, respectively, for a 16/84 wt% mixture of Loctite and propellant.

curve B, has an initial heat production of about 40 μW per gram, which levels off gradually. This heat is ascribable to a slow curing reaction, which is effectively suppressed through interference with the oxygen in the ampoule. Curve C is a calculated theoretical heat flow curve for a 16/84 mixture of adhesive and propellant with no chemical or physical interaction between the components ("non-interaction curve"). It is simply a 16/84% linear combination of B and A. The experimental behaviour of the mixture is illustrated by curve D, which differs markedly from curve C, indicating a certain level of interaction between the materials. There are two distinguishable interactions responsible for this discrepancy. First, the sharp peak after approximately 1 day is identified as a complete curing of a small fraction of Loctite, located in the perforations in the propellant grains, and thus protected from exposure to oxygen. Secondly, the shape of the rest of curve D is typical for an absorption process, in this case presumably swelling of the nitro¬cellulose in Loctite. The initital sorption rate is high due to large concentration gradients in the nitrocellu¬lose, but it decreases gradually when the system approaches equilibrium swelling. It is not possible to establish the existence of any chemical interactions accompanying the absorption. However, the merging curves C and D show that there are no long-term chemical effects of importance in the system.

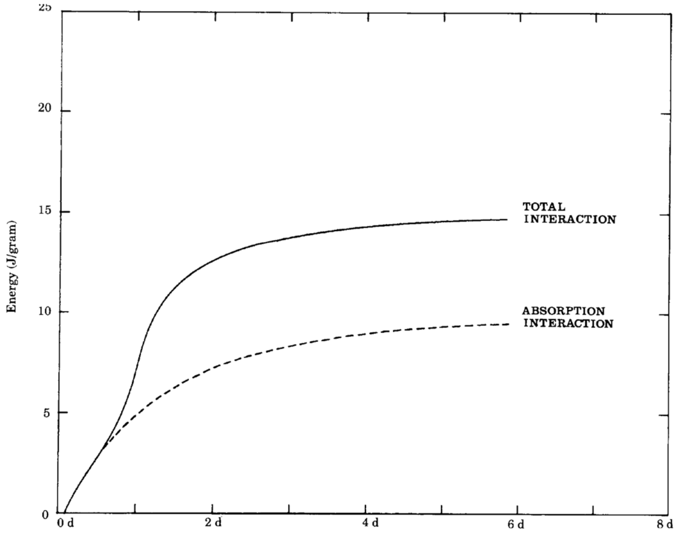

Fig. 2. Interaction energy vs. time for the Loctite 270/ single base propellant system. The dotted line is the estimated curve for the absorption process alone.

Integration of the difference between curves D and C with respect to time yields the interaction energy shown in fig. 2.

Interaction energies often provide valuable information about the type of interaction. The curing and "absorption" energies amount to approximately 5 and 10 J/g of mixture, respectively. The former is in good agreement with the calculated curing energy for the small volume of

Loctite in the perforations (3-4 J/g), and the latter corresponds to approximately 7 kJ/mole of nitrocellulose (monomer), which is a typical value for a physical absorption process rather than a chemical reaction.

Swelling effects and Loctite curing in perforations are phenomena that clearly affect the mechanical and burning characteristics of the propellant. Strictly according to the definition, the materials should there¬fore be classified as incompatible. We consider however, that this “functional” incompatibility is of little practical importance as long as minor amounts of the adhesive is used. Furthermore, no direct safety hazards are expected when the components are mixed, as indicated by the limited degree of interaction.

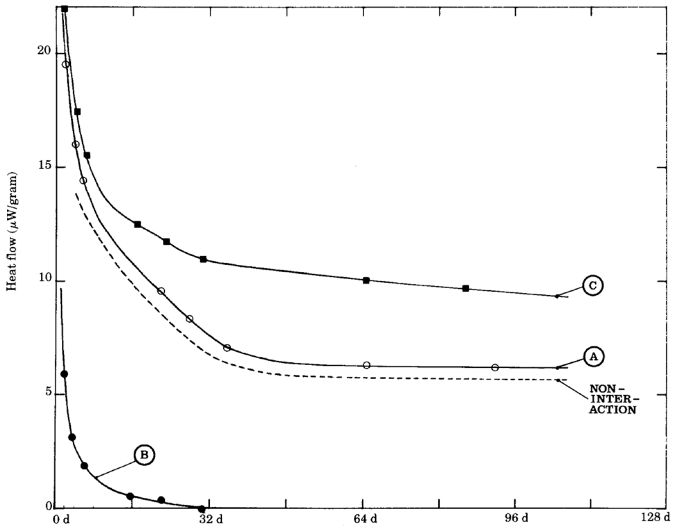

Fig. 3. Calorimetric curves for a 50% glass reinforced polyamid/single base propellant system. (A) propellant, (B) polyamide and (C) experimental curve for a 10/90 wt% mixture ofpolyamide and propellant.

Fig. 3 shows a compatibility study of a polyamide (50% glass fiber reinforced)/single base propellant system. In conformity with the first example, a non-interaction curve (dotted line) has been calculated for a 10/90 wt% mixture of finely ground polyamide and propellant. The corresponding experimental curve (C) is about 4 μW higher. This may look like a fairly weak interaction, but it is nevertheless important as it is practically constant over a long period of time. A considerable part of this interaction is supposed to take place in the polyamide between the amide groups of the polymer and propellant stabilizers absorbed by the polymer. A separate weight test has shown that the polymer increases its weight by 0.7% due to absorption of stabilizers. The stabilizer is a mixture of several nitro derivatives formed during the reaction with NOX in the propellant. In a previous study (5) we have shown calorimetrically that nitro groups may react strongly with amide functional groups. The interaction energy of the first 100 days amounts to approximately 600 J/g of polymer or 150 kJ/mole of monomer. This energy magnitude would correspond to a more or less complete degradation of the polymer if the interaction was mainly arising from a polymer backbone scission process. Since important changes in mechanical properties normally appear after only a few percent degradation, the polyamide must thus be considered as incompatible with this particular propellant.

Stability tests

As mentioned in the introduction, the microcalori-metric method could be used for stability testing of explosives. Some examples are shown in fig. 4.

Curve A represents a standard single base propellant. After approximately 4 days the propellant reaches a steady state at about 3 μW/gram at 70 °C. The heat production arises from the complex decomposition of the nitrate ester and the subsequent reactions between the liberated NOX gas and the stabilizer(s). The initial higher exotherm is presumably caused by interference with oxygen plus a number of equilibration processes when the sample temperature is raised from ambient to 70°C. The NOX concentration increases in the propellant when the stabilizer is gradually con¬sumed. This has a catalytic effect on the decompositions rate, and the heat production increases rapidly (autocatalysis). The phenomenon is clearly illustrated by curve B, which represents the same propellant without stabilizer. The catalyzed decomposition becomes evident after only 50 days, while there is practically no sign of increased rate during the first four months for the stabilized material.

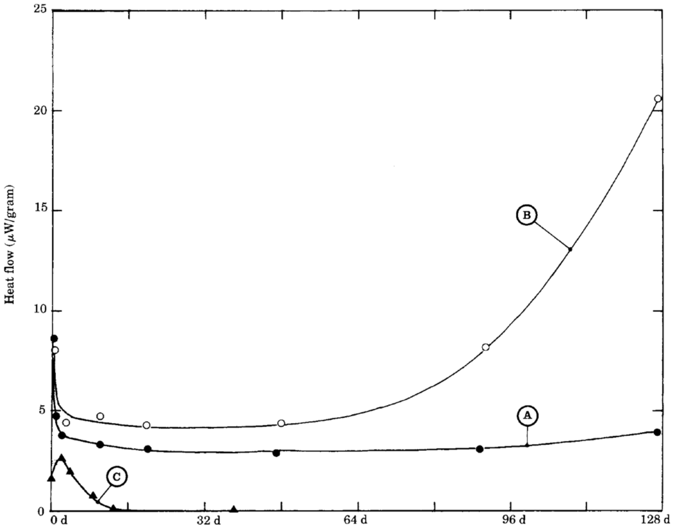

Fig. 4. Calorimetric curves illustrating the decomposition of a single base propellant (A) with and (B) without stabilizer. (C) represents a nitro compound (RDX).

The rate constant for the decomposition of a propellant is approximately changed by a factor 3 per 10°C (6). Since the sensitivity of the microcalorimeter is approximately 0.1 μW, it would thus be possible to measure the stability of the propellant in fig. 4 at least at 60°C and possibly even at 50°C, if statistical evaluation methods are employed. The time to autocatalysis for this propellant at 50°C, if statistical evaluation methods are employed. The time to autocatalysis for this propellant at 50°C is typically 25 years. The fact that it is experimentally possible to measure such a slow degradation process with some accuracy clearly demonstrates the excellent sensitivity of the instrument.

For comparison, the heat flow curve of a nitro compound (RDX) is also shown in fig. 4, curve C. This material has a negligable heat production, which indicates a very good stability at 70°C. A similar result has previously been obtained for a TNT sample (5).

Boron is frequently used in pyrotechnic compositions as a reducing agent. The pure material is readily attacked by oxygen (5), forming a layer of B_2O_3 on the surface. The large enthalpy of oxide formation (AH = -1262 kJ/mole) is of course favourable for calorimetric measurements, especially at low oxidation rates. An example of an oxidation process at 70°C in a consolidated igniting composition containing boron is presented in fig. 5.

Curve A represents the sample when exposed to a dry oxygen atmosphere in the ampoule. 3 hours after insertion in the calorimeter, the heat flow reaches a maximum at nearly 1400 μW/gram, followed by an immediate rapid decrease. Curve B illustrates an identical sample under dry nitrogen conditions. This curve exhibits only a small peak, probably due to an oxygen residue present in pores in the sample, or adsorbed on the surface of the components. Integration of the O_2 curve from 0 to 4 days yields a reaction energy equal to 62 J/gram, which corresponds to an oxygen consumption of 1.7 ml. This is approximately equal to the volume of O_2 in the ampoule, i.e. all oxygen has been used in the oxidation process. The heat flow would probably have continued at a high level if an unlimited quantity of oxygen had been accessible to the sample (a flow system must be used to verify this assumption).

A simple calculation shows that a constant heat flow equal to 1400 μW (= peak height) would correspond to oxidation of approximately 1% of the boron per day in O_2 at 70°C. The time for a 1% oxidation in air at room temperature would roughly be 1.5 years. Oxidation of 5-10% of the boron is probably sufficient for unacceptable changes in the burning characteristics of the igniting composition. This shows that oxidation processes could be an important ageing factor under special environmental conditions.

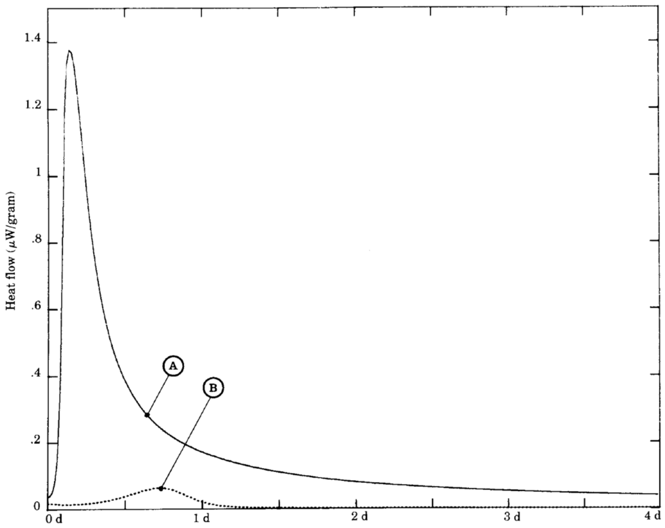

Fig. 5. Oxidation of boron in an igniting composition, (A) in dry oxygen and (B) in dry nitrogen.

CONCLUSIONS

Microcalorimetry is a very general method that could be applied to a variety of compatibility and stability problems of different physical and chemical natures. It offers an excellent sensitivity, which is indispensible e.g. for measurements of propellant decomposition rates at low temperatures and for establishment of long-term incompatibility between materials. In compatibility testing, heat flow data are used together with calculated interaction energies and physical and chemical considerations in the interpretation of in¬teraction phenomena. The microcalorimetric method is also well adapted for studies of oxidation and other surface reactions in pyrotechnic compositions.

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