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THERMAL STUDIES TO DETERMINE THE ACCELERATED AGEING OF FLARES

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Thermal analysis is an interesting technique to determine kinetic parameters of separate components, and also of a complete system to receive adequate information on the ageing process of pyrotechnic compositions. The investigated tracer is a tracking tracer of a Swiss missile. It is attached to a missile and produces during burning a red flame. The missile system is already in use for 15 years. Periodic inspections of the system take place every three years. These inspections, however only give information on the actual state of the tracer and not on the future state. The aim of this investigation is to predict the ageing behaviour of the tracer system to give additional information about the future use of the missile system.

After two ageing profiles the tracer systems were tested on the test range at Armasuisse in Thun. The results of the testing show that an ageing period of 4 weeks at 60°C gives no changes in performance (light output and burning time). On the other side also a quite heavy ageing period of 4 weeks at 150°C was applied on tracer systems, which gives a dramatically change in burning time. The light output was even higher after this ageing profile, although the intensity changes a lot.

Keywords: *kinetic analysis, lifetime studies, thermal analysis, tracer*

Introduction

The first part of the study was focused on a literature survey to look for the most critical components in the tracer system. Later on ageing experiments were performed in order to model the ageing of the most critical component as a function of temperature. These results were the input for the ageing program, where the tracer system was aged at an accelerated rate for a period corresponding to 15 years of storage, after which the system will be tested.

It is agreed to assume that the missile systems are stored in such a way that moisture will not enter the system. Therefore the influence of external moisture on the ageing behaviour was not investigated. The so-called acceleration factor of the tracer system was determined. This factor is needed to calculate the time necessary for the accelerated ageing experiments at high temperature to simulate the ageing during 15 years of storage.

The aged tracers were tested at the set-up in Switzerland, where also the periodic inspections were performed. The advantage of using the well-known equipment was that it can be checked whether the tracer system still meets the requirements, and the obtained data can be compared with data already obtained in the past from previous measurements done by the Swiss Ammunition Surveillance Organization. If the tracer system will still meet the requirements, it can be assumed that the tracer system will function well for the next 15 years if stored under the specified storage conditions.

The chemical properties and possible reactions of each ingredient of the composition are of course well-known under several conditions and are reported widely [1–10]. However, no literature was found focusing on the ageing aspects of this particular composition. Reactions found in literature on titanium/strontium nitrate composition were all from ignition or combustion studies, and from thermal analysis studies investigating the exothermic reactions in the region of 300–700°C.

Influence of the alloprene binder

The binder alloprene is a chlorinated latex rubber with the empirical formula $C_{10}H_{11}C_{l7}$. It plays an important role in the chemical reactions of the investigated pyrotechnic system. Upon heating, the binder decomposes. There are many species involved in the decomposition of alloprene. Evolved gas studies show the release of hydrochloric acid and many low molecular mass chlorinated hydrocarbons, the largest of which are species that correspond to the formula $\{C_2C_{l5}\}$. Methane is also detected in the evolved gases. At higher temperatures aromatic hydrocarbons are formed.

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$$\text{alloprene} \rightarrow HCl(g)+CH_4(g)+C_xH_yCl_z(g)+\ldots+\{\text{carbonaceous residue}\}(s) \qquad (1)$$

The released hydrochloric acid can react with the nitrate group to form nitrogen dioxide and strontium chloride:

$$Sr(NO_3)_2\,(s)+2HCl(g) \rightarrow SrCl_2(s)+ +2NO_2(g)+0.5O_2(g)+H_2O(g) \qquad (2)$$

Immediately, also nitric oxide is formed according to the nitrogen dioxide/nitric oxide equilibrium:

$$2NO_2(g) \leftrightarrows 2NO(g)+O_2(g) \qquad (3)$$

The nitrate/hydrochloric acid reaction occurs at a temperature of 300°C in thermogravimetry-differential scanning calorimetry experiments where samples are heated at a rate of $10\ K\ min^{-1}$, but it is reported that the reaction can readily take place at temperatures as low as 180°C.

Water is formed in the nitrate/hydrochloric acid reaction, and although strontium nitrate is not as hygroscopic as other nitrates it is hygroscopic above a relative humidity of 70%, affecting the ignitibility and the burning properties of the composition.

$$Sr(NO_3)_2(s)+nH_2O \rightarrow Sr(NO_3)_2{\sim}nH_2O(s) \qquad (4)$$

The carbonaceous residue of the alloprene binder absorbs nitrogen dioxide through chemisorption. At higher temperatures (but already at temperatures as low as 150°C), the reactive carbonaceous residue is oxidized by nitrogen dioxide:

$$1.5C(s)+2NO_2(g)+0.5O_2(g) \rightarrow +1.5CO_2(g)+2NO(g) \qquad (5)$$

The nitrogen dioxide and oxygen are provided by the nitrate/hydrochloric acid reaction, but nitric oxide can also be reduced:

$$C(s)+2NO(g) \rightarrow N_2(g)+CO_2(g) \qquad (6)$$

At even higher temperatures, strontium nitrate can be reduced by the carbonaceous residue to form strontium carbonate. Strontium carbonate then decomposes into carbon dioxide and strontium oxide.

$$C(s)+Sr(NO_3)_2(s) \rightarrow SrCO_3(s)+NO_x(g) \qquad (7)$$

$$SrCO_3(s) \rightarrow CO_2(g)+SrO(s) \qquad (8)$$

Reactions of nitrate

At elevated temperatures nitrates decompose. Partial decomposition leads to the formation of strontium nitrite and oxygen, complete decomposition to strontium oxide, nitric oxide and oxygen.

$$Sr(NO_3)_2(s) \rightarrow Sr(NO_2)_2(s)+O_2(g) \qquad (9)$$

$$Sr(NO_3)_2(s) \rightarrow SrO(s)+2NO(g)+1.5O_2(g) \qquad (10)$$

Reaction (10) is accompanied by the nitrogen dioxide/nitric oxide equilibrium (Eq. (3)). All oxides of nitrogen can eventually be reduced to molecular nitrogen:

$$NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (11)$$

It is known that pyrotechnic compositions containing a nitrate and magnesium age in the presence of water: hydrogen is developed in the reaction of magnesium and water and reduces the nitrate to an oxide, which then can react further to a carbonate in the presence of water and CO_2. Without the presence of magnesium, these reactions will take place given the proper reducing agent and the presence of water and CO_2.

$$Sr(NO_3)_2 \xrightarrow{\text{reduction}} SrO+NO+NO_2+O_2 \qquad (12)$$

$$\xrightarrow{H_2O} Sr(OH)_2 \xrightarrow{CO_2} SrCO_3+H_2O \qquad (13)$$

The presence of water (reaction (2)) can lead to a new series of reactions of the NO_x products: nitrogen dioxide is a mixed acid anhydride and can react with water to give a mixture of nitrous and nitric acids.

$$2NO_2(g)+H_2O(l) \rightarrow HNO_2(aq)+HNO_3(aq) \qquad (14)$$

The reaction products are denoted as ‘*aq*’ because in literature this reaction is described as taking place in solution. It is included in the list of all possible reactions because the species involved in the reaction could all be present. The same goes for the following step: upon heating, nitrous acid decomposes to give nitric acid and nitric oxide.

$$3HNO_2(aq) \rightarrow HNO_3(aq)+2NO(g)+H_2O(l) \qquad (15)$$

Nitrogen dioxide can also react with water and oxygen to produce nitric acid:

$$4NO_2(g)+2H_2O(l)+O_2 \rightarrow 4HNO_3(l) \qquad (16)$$

Reactions (1) to (16) can occur with and without the presence of titanium. Up to temperatures of 300°C titanium does not react with oxides of nitrogen or hydrochloric acid. However, the presence of titanium does however seem to enhance the oxidation of the carbonaceous residue of alloprene, it is assumed by increasing the potential of the gas-solid interaction.

Reactions of titanium

Titanium metal is resistant to corrosion. Only extremely small titanium particles (nanoscale) are highly reactive, a behaviour as most nanoscaled metal particles show. The sensitivity of these particles can be tuned by the thickness of the oxide layer on the particle. Titanium metal is coated with an oxide layer that usually renders it inactive at standard conditions:

$$Ti(s)+O_2(g)\rightarrow TiO_2(s) \quad (17)$$

The titanium oxide layer protects the metal from being oxidised completely. Compositions containing titanium are therefore far less reactive or sensitive to corrosion than compositions containing for example magnesium.

Thermal studies have shown that titanium does not react with water at temperatures up to 70°C. It is known that titanium will react with steam to form titanium oxide and molecular hydrogen:

$$Ti(s)+2H_2O(g)\rightarrow TiO_2(s)+2H_2(g) \quad (18)$$

Titanium will not react with hydrochloric acid at room temperature, but it can react with hot hydrochloric acid to form titanium(III) complexes:

$$2Ti(s)+12HCl(aq)\rightarrow$$
$$\rightarrow 2[TiCl_6]^{3-}(aq)+3H_2(g)+6H^+(aq) \quad (19)$$

This reaction requires the hydrochloric acid to be dissolved in water, and will therefore only take place, after water is formed in reaction (2) and if enough heat is generated.

Ageing of the titanium/strontium nitrate composition

Proposed mechanism

TG-DSC experiments show that the same reactions occur in binary alloprene/strontium nitrate compositions and ternary titanium/strontium nitrate/alloprene compositions. Titanium clearly does not play a chemical role in pre-ignition reactions. However, titanium does enhance the decomposition of alloprene and thus the release of hydrochloric acid. Also it enhances the amount of carbon dioxide being released, indicating a physical influence on the oxidation of the carbonaceous residue of the alloprene binder.

In thermal analysis studies, the mass loss of ternary compositions increases with increasing binder content. Therefore it seems likely that from all reactions investigated, the decomposition of the binder and the following reaction of its reaction products with the nitrate are the most likely reactions to occur as a result of ageing. It should be stated that these reactions take place without the presence of water.

The proposed mechanism is:

$$\text{alloprene}\rightarrow HCl+\ldots+\{\text{carbonaceous residue}\} \quad (1)$$

$$Sr(NO_3)_2+2HCl\rightarrow SrCl_2+2NO_2+0.5O_2+H_2O \quad (2)$$

$$2NO_2\rightarrow 2NO+O_2 \quad (3)$$

$$1.5C+2NO_2+0.5O_2\rightarrow 1.5CO_2+2NO \quad (5)$$

$$C+2NO\rightarrow N_2+CO \quad (6)$$

The reaction of nitrate with hydrochloric acid will be slow since it is endothermic. In DTA experiments however an overall exothermic reaction is observed. This is because the oxidation of the highly reactive carbonaceous residue of alloprene is strongly exothermic and is imposed on the endothermic reaction. The limited access of NO_x to the decomposing alloprene is thought to be the cause for the low level of oxidation of the highly reactive carbonaceous residue. Preliminary experiments have shown that the oxidation process is increased by confinement of the evolved gases.

Determination of critical parameters

A function and failure analysis is a tool to be used for the determination of the most critical components of the tracer with respect to ageing. Those components will be selected for artificial ageing experiments and modeling. In order to perform a function and failure analysis the exact build up and functioning of the tracer has to be known as well as data of aged tracers. This information is from periodic inspections available. The function and failure analysis is performed using information gathered from the disassembly of the tracer and from periodic inspection data of the Swiss Ammunition Surveillance.

Detailed description of the tracer

A tracer was disassembled in order to have a detailed description of its components and functions, and also to get material for investigations.

Figure 1 shows a schematic overview of the tracer. The end that is attached to the missile body is shown on the left side. The tracer consists of a steel case, an inert aluminium plug, a pyrotechnic pellet, and an end plug. The pyrotechnic charge is separated from the aluminium plug with a cardboard disc. For ignition a pyrotechnic igniter cord is fitted to the end plug.

An igniter cord runs through the rubber end plug and comes in direct physical contact with the pyrotechnic pellet (Fig. 2). The composition of the igniter cord consists of boron and potassium nitrate. Two wires run through the cord for heat conduction. This kind of cord produces a very hot gassy flame that ignites the pyrotechnic pellet.

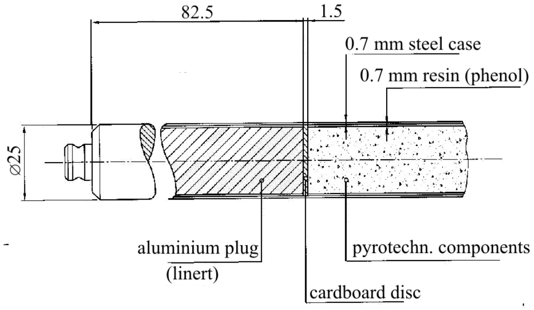

Fig. 1 Schematic overview of the tracer

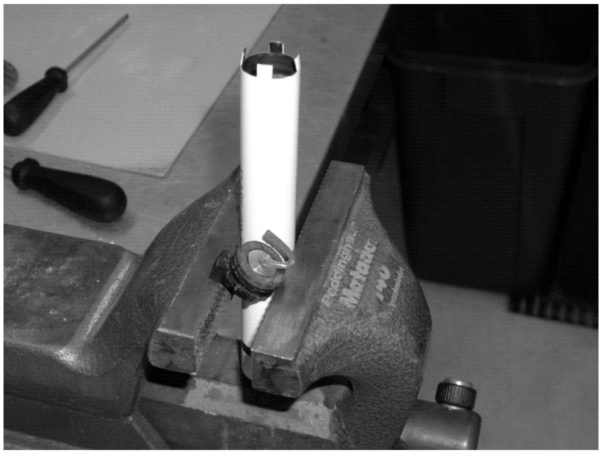

Fig. 2 End plug with igniter cord removed from (end plug not shown) the top of the tracer

Experimental

Used techniques

For the determination of the kinetic parameters thermogravimetry analysis combined with DTA (differential thermal analysis) is applied. Thermogravimetry analysis (TG) is a technique in which the mass of a substance is measured as a function of temperature by subjecting the substance to a pre-set temperature program. The mass is continuously monitored with a thermobalance. A sample of the substance is put in an oven, which can either be kept at a constant temperature or be heated up with a pre-set heating rate. The test equipment is also capable to measure changes of energy by (DTA). The big advantage of this technique is the fast way to perform kinetic analysis of energetic materials.

Kinetic investigations on tracer material

The kinetics, e.g. activation energy can be calculated in different ways. For this study two methods are used,

- modified Kissinger method
- model-free kinetics method

There is a preference to use a model-free method, because from this method a graph of the activation energy as a function of temperature can be calculated. In this case more processes are affecting the decomposition, a non-linear curve will be obtained.

The tracking tracer system can be divided in four different parts:

- grey composition
- black composition
- phenol resin
- stopper

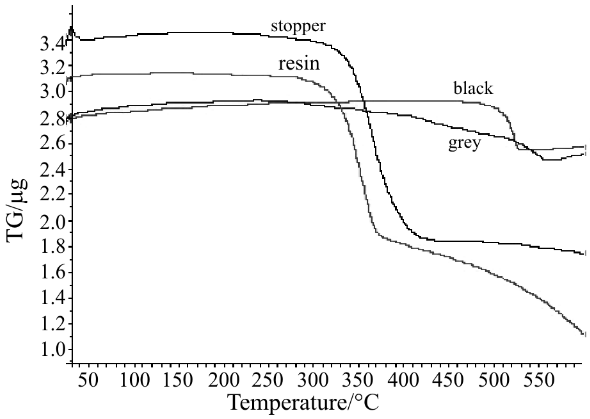

Fig. 3 TG measurement on four separate components (5 K min^{-1})

The first indicative experiment has been performed on the four separate components. The tests are performed with a heating rate of 5 K min^{-1} under an air atmosphere.

The results of these measurements are presented in Fig. 3. From this figure it can be concluded that the 'grey' and 'black' composition are the most stable ones. This is in line with the reference literature where is mentioned that the titanium/strontium nitrate composition is stable. The difference between the 'grey' and 'black' composition is the amount of alloprene. The 'grey' composition contains more alloprene which results in a small mass change at higher temperatures. The two additives, rubber stopper and the phenol resin, are less stable. The first step of the decomposition starts for both components at a temperature of about 300°C.

The heating of the system, conducted with 2, 5 and 10 K min^{-1}, gives the mass losses as shown in Fig. 4.

As it appears, there are two steps of mass loss: the first process begin around 250°C and goes until around 350°C; the second process starts around 400°C and goes continuously until the end of the recording (594°C). The first process is those of interest, being related to the degradation of the epoxy resin.

After separating this process one obtains the conversion-temperature diagram for the three plots. Also one obtains, by derivation, the reaction rates for the three heating rates.

The kinetic analysis is based on these plots for the initial part, until 20% conversion, because at higher conversion rates the thermal equilibrium in the equipment is disturbed by the exothermal effects.

The activation energy, E

The values of activation energy through Kissinger

The peaks of reaction rate as in Fig. 7 can be used for calculating the activation energy of the whole process from the plot:

$$\ln(\beta/T_{\mathrm{p}}^2)\ vs.\ -1/RT_{\mathrm{p}} \qquad (20)$$

where β is the heating rate and T_{p} is the peak temperature. One obtains E=225 kJ mol^{-1}.

The kinetic parameters through Flynn–Wall–Ozawa and Friedman.

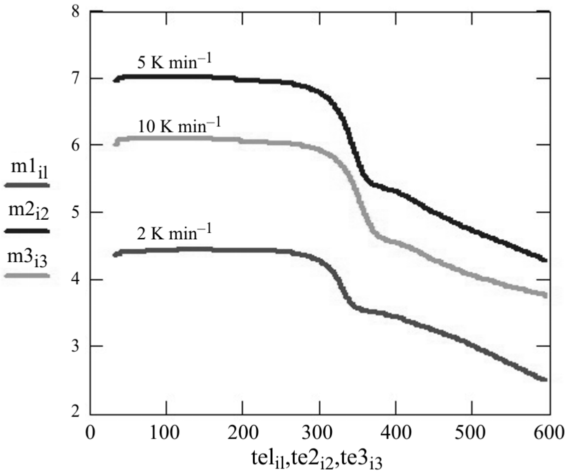

Fig. 4 The TG plots of the system heated with 2, 5 and 10 K min^{-1}

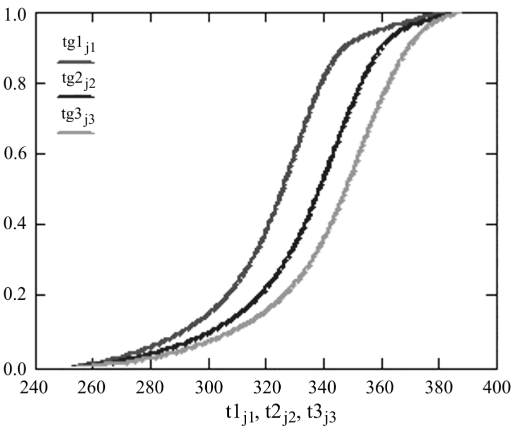

Fig. 5 Conversion-temperature plots

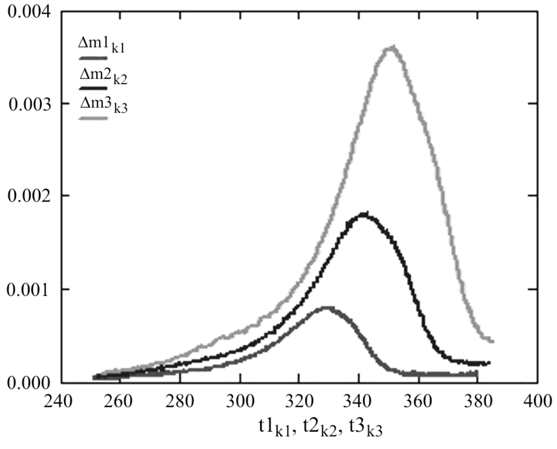

Fig. 6 Reaction rates

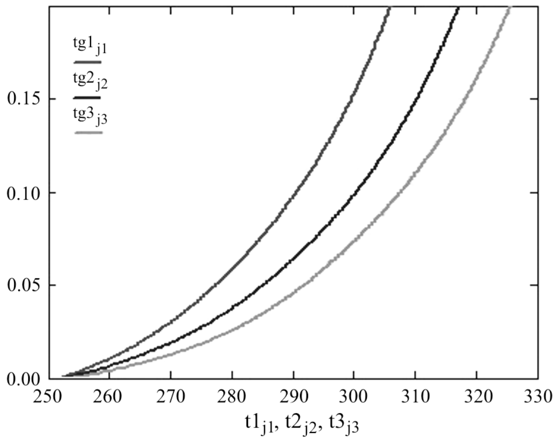

Fig. 7 Conversion *vs.* temperature for conversion up to 20%

Being an integral iso-conversional method, Flynn–Wall–Ozawa method uses the graphs of conversion *vs.* temperature. The plot of:

$$\ln\beta\ vs. -1/RT \qquad (21)$$

for temperature measured on each graph at the same conversion, gives values which start at 271 kJ mol^{-1} and decrease quickly to 230 kJ mol^{-1}, as shown in Fig. 8.

Being a differential iso-conversional method, Friedman method uses the graphs of reaction rate *vs.* temperature. The plot of:

$$\ln[(\mathrm{d}m/\mathrm{d}T)x\beta]\ vs. -1/RT \qquad (22)$$

for temperature measured on each graph at the same conversion, gives the activation energy.

In this case the values of activation energy range from 290 kJ mol^{-1} at the beginning, to 220 kJ mol^{-1}, the value where the activation energy seems to stabilise very quickly, as shown in Fig. 9.

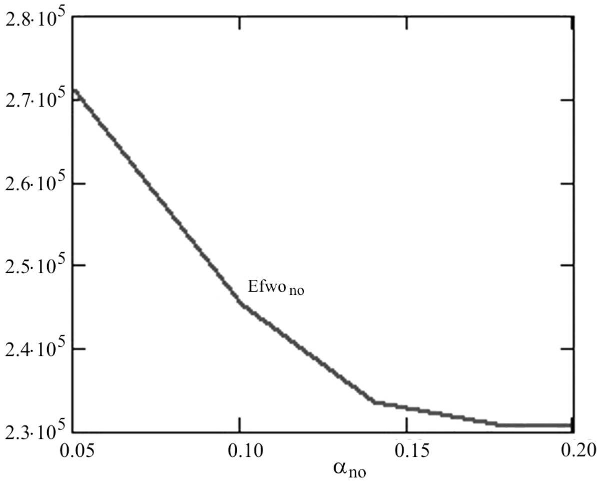

Fig. 8 The dependence of activation energy, calculated by Flynn–Wall–Ozawa method, with conversion

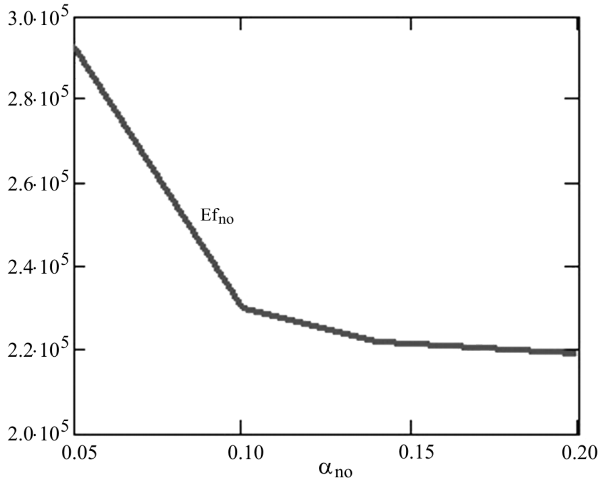

Fig. 9 The dependence of activation energy, calculated by Friedman method, with conversion

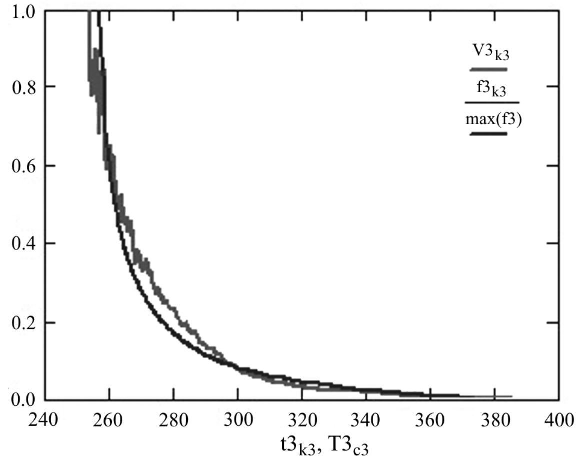

Fig. 10 The ■ – is the fitting function and the ● – are the experimental data

Summing up, the calculation of activation energy leads to E=225±6 kJ mol^{-1} as a good average.

The kinetic function, f(α)

Further on the analysis, based on the average value of E obtained in Fig. 9, one calculate the kinetic function which fits best the normalised plot of:

$$(\mathrm{d}m/\mathrm{d}T)/\exp(-E/\mathrm{R}T)\ vs.\ T \tag{23}$$

as shown in Fig. 10.

The best fitting was obtained for the kinetic function:

$$f(\alpha)=[-\ln(1-\alpha)]^{-0.7} \tag{24}$$

which is close to the 2D diffusional model (for which the power is –1, instead of –0.7). This means a cylindrical diffusion of gaseous products.

The pre-exponential factor, A

Based on the value of E and the kinetic function, $f(\alpha)$, it follows that: A=3·10^{16} s^{-1}.

Calculation of time for ageing

Now, the time required for any conversion, α, at any temperature, T, by using the equation, can be calculated;

$$\text{time}=\frac{\displaystyle\int_{0.00000001}^{\alpha}\frac{\mathrm{d}x}{[-\ln(1-x)]^{-0.7}}}{3\cdot10^{16}\exp\left(-\dfrac{225000}{8.31T}\right)}\frac{1}{3600}\frac{1}{24}\frac{1}{365} \tag{25}$$

In formula (25), the time is given in years. The integral equals to 3.653·10^{-3}, and the inferior limit should be taken different from 0 (and very close to 0) for avoiding the singularity.

With this formula it will notice that the time required for the epoxy resin to have conversion up to 0.1% (higher values results in malfunctioning of the article) is in the range of 10^4 years at 90°C. It is obvious that the resin is not aged at all during 15 years at 5–10°C. This result is confirmed, also, by the onset temperature, which is around 250°C, which is much higher than the assumed storage temperature.

One has to notice that the conversion function plays a little role for conversions below 5%, as any form gives an integral of the order of 10^{-3} and, therefore, does not change the order of time.

The time can be also calculated with the formula:

$$\text{time}=\frac{\displaystyle\int_{T_0}^{T_\alpha}\exp\left(-\frac{E}{Rz}\right)\mathrm{d}z}{\beta\exp\left(-\dfrac{E}{RT_{\text{ageing}}}\right)}\frac{1}{60}\frac{1}{24}\frac{1}{365} \tag{26}$$

The time is given also in years. This formula has the advantage it does not need the values of pre-exponential factor and of the kinetic function, as Eq. (25). It requires the onset temperature on the curve recorded at heating rate β, and the value of temperature at which is recorded at 0.1% conversion, $T_{0.001}$, on the same curve. Following by the calculation of the time required to age at the ageing temperature, T_{ageing}, between 60 and 90°C. The 'z' is the variable of integration.

Replacing the activation energy, E, with 225 kJ mol^{-1}, for T_0=523 K (250°C) and $T_{0.001}$=525 K (252°C) at heating rate of 2 K min^{-1}, one obtains time≈10^4 years for ageing at 90°C. This is in a good agreement with the value obtained by first formula.

Summarizing, this confirms indirectly that the kinetic of the beginning of epoxy resin decomposition reaction has the parameters:

$$E=225\ \text{kJ mol}^{-1}$$

$$A=3\cdot 10^{16}\ \text{s}^{-1}$$

$$f(\alpha)=[-\ln(1-\alpha)]^{-0.7}$$

Proposed ageing profile

As mentioned in the literature, and investigated in this study, the composition of titanium/strontium nitrate seems to be very stable. In the case of this tracking tracer, the limitation will probably be the phenol resin, which is located between the composition and the metal casing. To calculate the ageing profile the kinetic parameters from combinations of the grey composition and the resin are used.

Based on the kinetic results, the following ageing profiles are proposed and performed:

4 weeks @ 60°C and 4 weeks @ 150°C

Both ageing profiles are performed with the complete article, which means that the ageing is influenced by the atmosphere (air) inside the article. The explanation for these two profiles is as follows.

4 weeks @ 60°C

a maximum temperature which, could be expected during different ‘hot-area’ operations.

4 weeks @ 150°C

Although the kinetic studies gives no indication of stability problems (e.g. conversion of the main components), a very extreme ageing profile is supplied to the tracking tracer, to investigate the influence of temperature on the functionality. This profile is comparable with more than 100 years at a storage condition of 10°C.

Firing experiments

To investigate the worst case scenario, the four tracking tracers, aged for 4 weeks @ 150°C are also investigated. Based on the results it could be concluded that this artificial aged tracking tracers will not pass the criteria for the t_2–t_1 value (illumination period of the tracer system), which has to be more than 18 s. The burning characteristics of these artificial aged tracking tracers were very intensively, short and sometimes parts of the tracer composition were spread out. Strange enough the light quantity will still fulfil the criteria of a value of more than 200 000 (Fig. 11).

Based on Fig. 12, the artificial ageing period for 4 weeks at 150°C were too extreme.

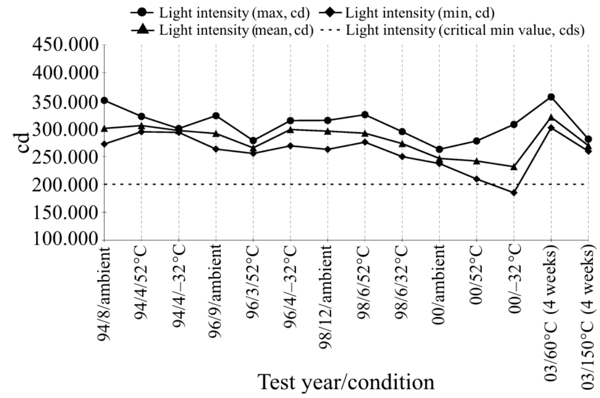

Fig. 11 Trend analysis on the illumination period (s)

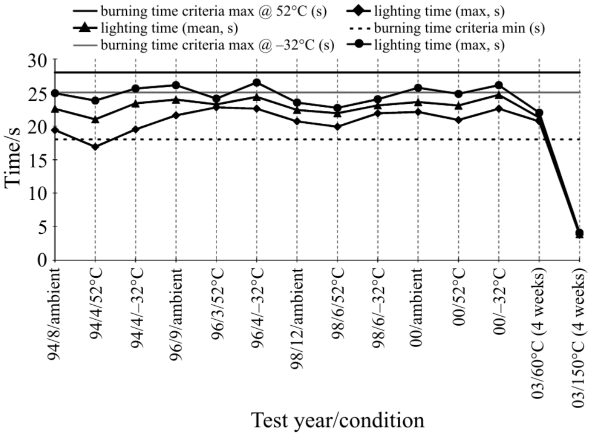

Fig. 12 Trend analysis on the burning time (s)

In the following hypothesis an explanation is given for the strange event that the burning time becomes too short and the light quantity is still above the criteria.

During the ageing period a mass loss of about 1.1 *m*% instead of the value of 0.06 *m*% after the ageing period at 60°C. This mass loss is probably caused by the decomposition of the phenol resin (start of decomposition at 308°C).

This phenol composition has the lowest decomposition temperature. And a long isothermal ageing period at 150°C will already give some conversion. This conversion makes the resin weaker, and during the firing a flash-over from the front line to more inside the tracer very well possible. This explains the fact that the light quantity will be in the same range (no large amount of material is lost) and the burning time will be much shorter. After this ageing period an uncontrolled burning profile takes place.

Conclusions

Based on the information of the periodic inspections, the ignition charge comes out as the critical function of the Swiss tracking tracer in the function and failure analysis, and possibly the burning of the main charge.

From thermal studies and thermodynamic calculations it is found that the proposed mechanism of the ageing of the titanium/strontium nitrate/alloprene composition is an exothermic process. If this process occurs it can have an influence on the ignition and burning properties of the composition, like not igniting, shorter burning times or low intensities.

Not igniting or burning is not observed in the periodic inspections. A low intensity is observed in the case of one particular lot. A short burning time is observed in two cases.

Because there is little information from consecutive periodic inspections of the same lot over a period of time, it is not known if all the abnormalities observed in the periodic inspections are a result of ageing. The abnormalities observed in the periodic inspections can in any case all be brought back to the pyrotechnic item consisting of the main charge and the ignition charge. In the next phase of the project, the two pyrotechnic compositions will be the subject of artificial ageing experiments. The interaction with the phenol resin they are pressed into will also be investigated.

It was decided to use the identified activation energy (225 kJ mol^{-1}) for the accelerated ageing tests. The period for accelerated ageing corresponded with 7.5 and 15 years of ageing under storage condition (in the original proposal it was suggested to age only corresponding a period of 15 years of ageing).

Ageing under very extreme conditions (4 weeks @ 150°C) results during the firings in a light intensity which passes the criteria, but does not fulfill the burning criteria.

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