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Aging of Pyrotechnic Compounds with Infrared and Thermal Analysis

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Pyrotechnics are compounds that have low weight but have high internal energy. In this article, it is decided to understand the age of samples of pyrotechnic that have maleonitrile. The infrared and thermal analysis were performed for identification of samples differences.

Key Words: Aging, Pyrotechnic, Infrared, Thermal analysis, Explosive, Propellant, High energy materials.

INTRODUCTION

The expression pyrotechnics comes from the Greek words 'Pyros' and 'Techne'[1]. Pyros ——→ fire, heat and Techne ——→ art. Pyrotechnics is one of three closely related subjects, high explosive, propellants and pyrotechnics itself. These three subjects not only have a common physico-chemical background, their functions and purposes also overlap. An excellent representative for this statement is black powder. In this typical manifestation, explosives perform at the highest reaction speed, leaving gaseous products. Propellants produce gas at moderate rate and pyrotechnic compositions react mostly at visibly observable rates, producing solid and liquid reaction products as well as gases[2,3]. The basis of pyrotechnic reaction can be displayed generally as follows:

Reducing agent (1) + Oxidizer (2) ——→ Redox reaction ——→ Oxidizer (1) + Reducing agent (2)

During the redox reaction, the reducing agent (fuel) is oxidized and the oxidizer is reduced. The pyrotechnic reaction is mostly a solid-solid, solid-liquid or solid-gas state reaction. To predict the reaction behaviour of a pyrotechnic composition, it isn't or only partly possible to apply inorganic chemistry theory which is based on chemical redox reactions in solutions. Pyrotechnic reactions are high-temperature redox reaction they take place in a temperature range of 1500-4000 °C. Due to this fact also the reaction products of a pyrotechnic redox reaction are in most cases not the same as expected according to classical chemical theory[4]. Additional pyrotechnic compositions contain auxiliary supplies. Due to the large variety of auxillary supplies it is not possible to present a detailed overview in this paper. To produce different coloured light emissions, it is necessary to have auxiliary substances in a pyrotechnic composition. Very often such substances have a double function, they act on one hand as an oxidizer and on the other hand they are responsible for producing coloured light during the redox reaction. Some famous emitters of coloured light are the oxides or nitrates of sodium, potassium, barium, copper and strontium. To produce pyrotechnic compositions, it is important to use well-defined chemical products. The following important parameters for chemicals used in pyrotechnics must be known: (a) Purity, (b) Particle size, (c) Particle shape, (d) Particle surface, (e) Crystal structure, (f) Water content.

There are several types of oxidizers and reducer agents with different relativities available, *e.g.*, KNO_3, $BaNO_3$, $KClO_4$, $NaNO_3$ and zirconium, titanium, silicon and boron. More pyrotechnic compositions are mixtures consisting of very fine powders. To produce granules it is necessary to add binders. Different types of binders are in use: natural product *e.g.* acaroids resin, Arabian rubber, semi synthetic products *e.g.* cellulose nitrate, dextrin, synthetic products *e.g.*, polyvinyl chloride (PVC), polynitro polyphenylene (PNP), polyglyn, polynimmo and other polymers[5,6].

Manufacturers of pyrotechnic compositions normally give a lifetime guarantee of 5 to 7 years. The following parameters influence the aging of pyrotechnic compositions: (i) Humidity, (ii) Temperature, (iii) Time.

Many pyrotechnic redox systems contain magnesium as a reducing agent. Magnesium is very sensitive to humidity. Fig. 1 shows the reaction mechanism of magnesium and water[7,8]. It was observed that the reaction products $Mg(OH)_2$ and MgO lead to an increase in volume due to their higher density. This increase in volume is frequently responsible for failures of pyrotechnic components.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2 \quad (1)$$

$$Mg(OH)_2 \longrightarrow MgO + H_2O \quad (2)$$

Fig. 1. Reaction of magnesium and water

Barisin *et al.*[9] determined the aging of pyrotechnic by X-ray. The physical and chemical characteristics of green signal pyrotechnic mix, before and after destabilization caused by the action of increased humidity at different temperatures, were determined. Data obtained by the means of X-ray diffr-action. IR spectroscopy and adiabatic calorimetry were compared with the results acquired by measuring functional characteristics (the dominant wavelength and the colour due of the emitted light, the intensity of the emission and the rate of burning). Comparison of all of these results points out to the very close relationship between the X-ray diffraction data and the function of the signal mix. Chemical changes, leading to the disuse of the examinated mix, were recognized as $Mg(OH)_2$, $BaCO_3$ and $Ba(NO_2)_2$ formation with concomitant decrease in Mg and $Ba(NO_3)_2$ content. Since no changes were observed in separately aged components, the interaction among components proved to be of essential importance[9].

After that Barisin and Batinic-Haberle[10] determined the aging of special pyrotechnic by IR and X-ray. The aging of tracers, containing different amounts of Mg, $Sr(NO_3)_2$, $KClO_4$, Al-Mg alloy and organic binder, was conducted under the conditions of 50.0 % and 98.5 % relative humidity's at 75 °C and of 98.5 % relative humidity at 25 °C. IR spectroscopy and X-ray diffraction were used for investigation of chemical changes. At the lower humidity no detectable changes were observed. Tracer of metal oxidant ratio > 1 exhibits decreased stability, changing significantly under the conditions of higher humidity, even at room temperature. In the reaction sequence of aging process ($Mg(OH)_2$) and $SrCO_3$ are formed, with concomitant decrease in Mg and $Sr(NO_3)_2$ content. Alloy changes only slightly and the content of $KClO_4$ and binder remains unchanged. Interaction between metal and nitrate is considered to be essential in the process of chemical aging[10]. In this paper, the aging of pyrotechnic component by infrared and thermal analyses were performed.

EXPERIMENTAL

Thermal analysis was done by PL-STA 1500 with heating rate 5 °C/min and air atmosphere and Perkin-Elemer 1710-FT IR with 4 cm^{-1} resolutions.

Four samples of pyrotechnics that had 2 g weight and had lactose, calcium carbonate and Cs (*ortho*-chlorobenzilidene maleonitrile) and potassium chlorate.

The sample 1 was treated by 98.5 % humidity and 25 °C, the sample 2 was treated by 98.5 % humidity and 100 °C, the third sample was treated by atmosphere humidity and 25 °C, the last sample was in atmosphere temperature and humidity.

RESULTS AND DISCUSSION

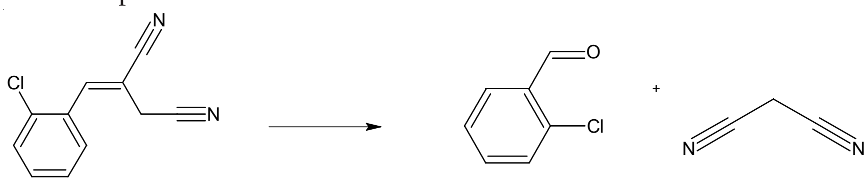
For determining of destroying temperature of pyrotechnic samples, first DTA analysis was done and the endothermic curves showed that at 100 °C temperature the pyrotechnic sample was destroyed.

After 10 d treating of samples with above conditions it was analyzed by infrared and thermal analyses. Before treating the samples, the FT-IR spectrum of samples were prepared. The absorptive bonds in 620, 1052, 3700-2960 and 2032-1440, 2230, 1590, 1130, 760 cm^{-1}, which respectively related to perchlorate, carbonate, C=O bonds and nitrile groups and two substituted benzene ring. After treating all of samples, we analyzed the samples by FT-IR and the spectra showed bands at 2230, 1050 and 620 cm^{-1} which less than original sample. In sample 2 all of peaks height are less than original IR corresponded peaks, because the temperature and humidity were high (98.5 % humidity and 100 °C), the sample 1 only had high humidity so the compounds that affected by humidity were lactose and Cs, the IR spectrum of this two samples (1, 2) proved present prediction. The height of IR peaks is less than originals. $KClO_3$ in sample 2 wasn't changed, because for changing perchlorate needs to high temperature. But in sample 3 height of $KClO_3$ peak is changed. the others had no change. The decomposition of $KClO_3$ is as below:

$$2KClO_3 \longrightarrow 2KCl + 3O_2\uparrow$$

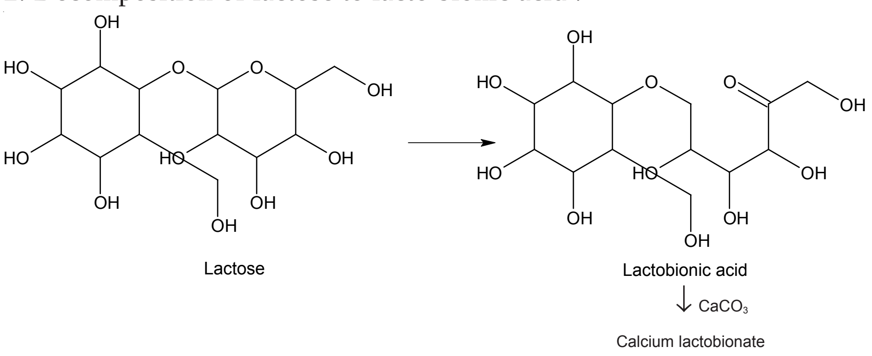
The sample 4 had IR spectrum as original ones. Now, the changes of Cs and lactose in pyrotechnic samples were analyzed. The lactose was changed to lacto bionic acid and because of calcium carbonate in samples that is basic, so the calcium lactobionate was prepared, as the height of COO^- absorptive peak in IR was shown, but in original spectrum of pyrotechnic the height of peak corresponds to CN group (2230 cm^{-1}) is bigger than in samples IR spectrum. The over all changes are shown below:

1: Decomposition of Cs:



Cs (*ortho*-Chlorobenzilidene maleonitrile)

2: Decomposition of lactose to lacto bionic acid :



The changes in samples 1, 2 and 3 are shown above.

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