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SEM/EDX AND FTIR/ATR BEHAVIOR OF AMMONIUM PERCHLORATE UNDER ACCELERATED AGING IN A NEW SOLID ROCKET MOTOR FUEL COMPOSITION WITH SUPERIOR EXPLOSIVE AND MECHANICAL PERFORMANCE

Alexandru MARIN*, Maria-Daniela SANDU*, George-Ovidiu IORGA*, Gabriel EPURE*, Dănuț MOȘTEANU**

***CBRN Defence and Ecology Research and Innovation Center, Bucharest, Romania**
****"Nicolae Bălcescu" Land Forces Academy, Sibiu, Romania**
alexandru.marin@nbce.ro, dmosteanu@gmail.com

Abstract: *The oxidation potential of perchlorates is high, which makes this material suitable for fuels with high specific impulse. Perchlorates are characterized by a ClO4- moiety/anion in their molecular structure and are crystalline materials used in the formation of solid fuels. Ammonium perchlorate (AP) particle size and shape influence the manufacturing process of fuels and their burning rate. The physical and chemical processes that can occur in the natural degradation process of composite fuels are related to molecular reactions and diffusion phenomena governed by kinetic processes and can be accelerated by increasing the temperature.*
The paper presents studies carried out by scanning electron microscopy and infrared spectrometry on the behavior of ammonium perchlorate in the new composite material of solid rocket motor fuel under the effect of high temperature, in the range of 65-85^{o}C, at regular time intervals. The self-initiation temperature was also determined, with a temperature rise rate controlled at 5^{o}C/minute.
It is very likely that these accelerated aging studies will show the changes that occur in the stability, sensitivity, mechanical and functional properties of fuels during their lifetime.

Keywords: ammonium perchlorate, scanning electron microscopy, infrared, self-initiation temperature

1. Introduction

Ammonium perchlorate is currently the most widely used oxidizer for solid rocket propellants in military and aerospace applications due to its excellent performance characteristics (high oxygen content, burning rate, specific impulse, density) and storage stability [1].

Within the project *Self-propelled pyrotechnic system for signaling and lighting with colored flame* (a grant of the Ministry of Research, Innovation and Digitalization), a series of composite rocket engine fuel compositions was developed, based on new generations of intelligent binders, with superior explosive and mechanical performance, under the conditions of reducing the risk associated with obtaining, handling and use, but also reducing the impact on the environment.

Preliminary studies on the behavior of oxidants in the composite fuel matrix was focused on the use of ammonium perchlorate, as a potential candidate, and experimental research was carried out by SEM/EDX and FTIR/ATR, regarding the evaluation of AP behavior in a solid fuel composition, based on PA, aluminum - fuel

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and a binder system synthesized from recycled polyethylene terephthalate (PET).
The purpose of the current experiments was to study the effect of high temperature on ammonium perchlorate in the new solid rocket motor fuel composition. Taking into account the investigation possibilities offered by scanning electron microscopy and the specific nature of the investigated materials, the characteristic X-ray spectra were acquired on the basis of which the chemical weight of the chemical elements contained in the material phase of ammonium perchlorate was expressed, in relation to aging parameters (time, temperature, humidity).
The optimal scanning current was determined, so that the investigated samples are not degraded following electron bombardment, a parameter that can damage the morphochemical structure through electrostatic charging and raising the investigation temperature and can affect the chemical stability of the sample by favoring some physical and chemical transformations, supported by electric charge and temperature. Relevant conclusions were formulated regarding the sizes of the oxidant particles that enter the structure of the tested materials: perimeter, diameter, area, deviation from sphericity.
Through infrared spectrometry with Fourier transform, specific functional groups of PA were monitored at the characteristic wavelengths. Before exposure to high temperature, the composition of the solid fuel was additionally investigated, so that the data acquired served as reference elements in the monitoring process. The auto-initiation temperature was also determined, with a temperature rise rate controlled at 5ºC/minute.

2. Accelerated Aging Method

Accelerated aging was performed at varied temperatures and exposure times. The accelerated aging temperature was chosen at a difference of 10°C. Thus, the stages of the accelerated aging process were carried out at 65°C, 75°C and 85°C (Table 1), using a DY-Angelantoni climatic chamber, with a programmable temperature controller in the -40÷+180°C range and a humidity controller programmable in the range 4÷44%. Fuel strips of 5x50 mm dimensions were cut from the fuel sample and placed in Duran-type glass vials with a tight closure.

3. Methods and Tests

3.1. Investigated Solid Fuel Composition

The studied composition of ammonium perchlorate-based composite fuel contains aluminum as fuel and a polymer-based binder added with various plasticizers and antioxidants. The investigated composition is coded PA01 and the reference, unaged composition is denoted PA01T0.

3.2. Accelerated Aging Conditions

Table 1 Accelerated aging conditions

Aging period @65°C	**Aging period @75°C**	**Aging period @85°C**
$PA01T_0$ (reference)		
Number of samples		
8	8	6
Days of accelerated aging		
3, 6, 9, 15, 17, 20, 22, 24	1, 2, 4, 7, 8, 9, 10, 17	2, 3, 4, 5, 7, 15

3.3. Experimental Measurements

SEM/EDX. Equipment: VEGA II LMU scanning electron microscope (SEM) equipped with a Bruker AXS X-ray dispersive (EDX) microanalysis unit using a QUANTAX 4000 model X-ray detector and an Xflash silicon drift (SD3) spectrometer. Operational parameters:

voltage 30 keV; optimal scanning current 20 ÷ 40 nanoamps; resolution 10 nm, pressure $50*10^{-2}$ Pa.

FTIR/ATR. The wavelengths attributed to the functional groups identified in the ammonium perchlorate molecule are: for the ammonium ion 1427 cm^{-1} (1417 cm^{-1} in the reference spectrum of the authentic compound) and 3281 cm^{-1} (3283 cm^{-1} in the reference spectrum) and for the perchlorate anion 625.4 cm^{-1} (623.4 cm^{-1} in the reference spectrum).

Equipment: Fourier transform infrared spectrometer FT-IR 6300, equipped with single reflection diamond crystal (ATR). Operational parameters: wavelength between 4000 - 400 cm^{-1}; resolution 4 cm^{-1}; number of points/purchase: 3630; incidence angle of 30^0.

4. Results and Discussion

4.1. SEM/EDX Analysis

Following the electronic scan, the chemical elements C, N, O, Al, Cl, Ni and Cu were identified and ammonium perchlorate appears as embedded as a distinct material phase (Figure 1), presenting dimensions in the range of 0.1-250 µm.

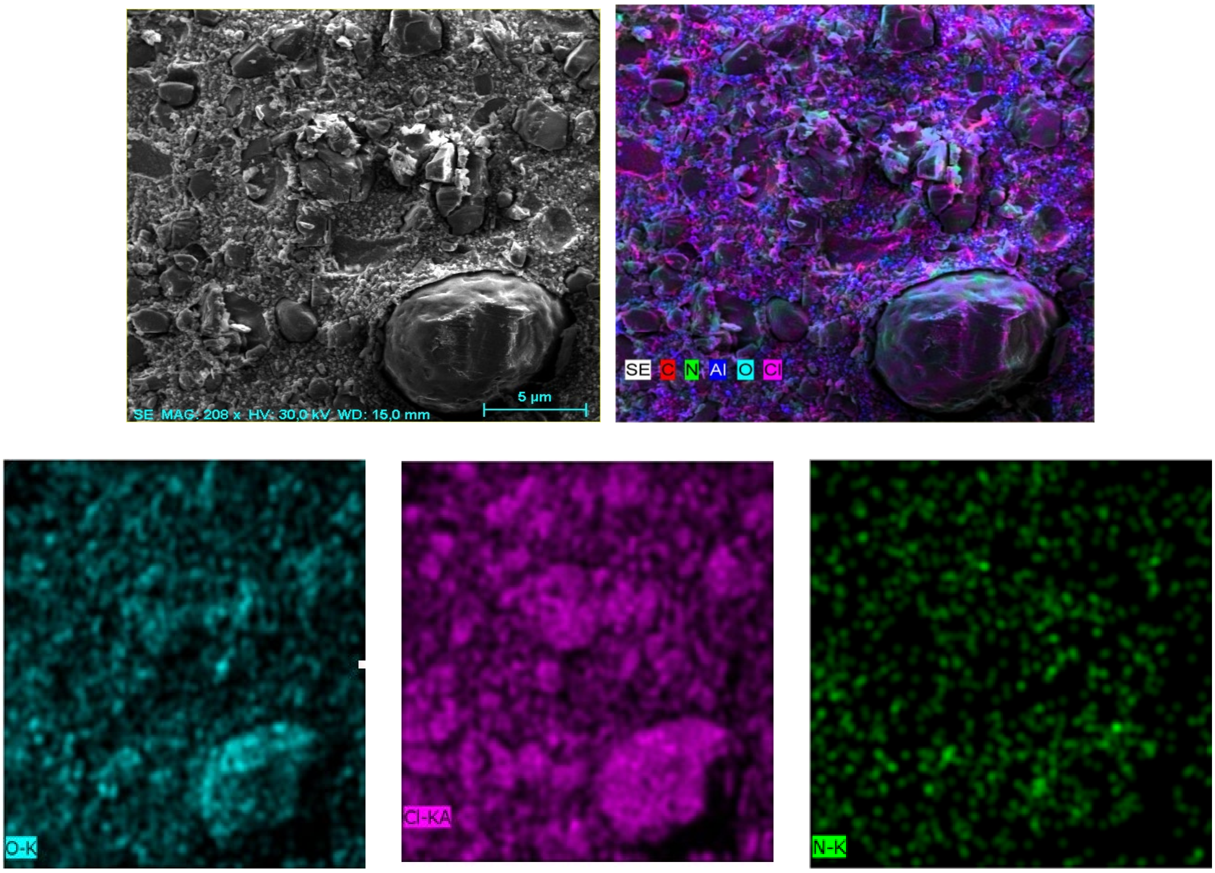

Figure 1: Morphology and morphostructure of AP01 composition

The variation of the content of chemical elements in the structure of the material phase with a majority content of ammonium perchlorate at the temperature of 65°C, 75°C and 85°C is presented in tables and graphs in Figures 2-4.

Days of accelerated aging	C_R %						
	Al	**C**	**N**	**Cl**	**Ni**	**Cu**	**O**
0 (Ref.)	0.00	0.00	0.00	88.46	0.00	0.00	11.53
6	1.30	0.65	1.30	84.31	0.00	0.65	11.76
9	1,22	0.61	1.84	79.75	0.61	0.61	15.33
20	2.00	0.00	2.00	86.00	0.00	2.00	8.00
22	3.22	1.61	1.61	74.19	0.00	0.00	19.35
24	2.22	0.00	2.22	86.66	0.00	2.22	6.66

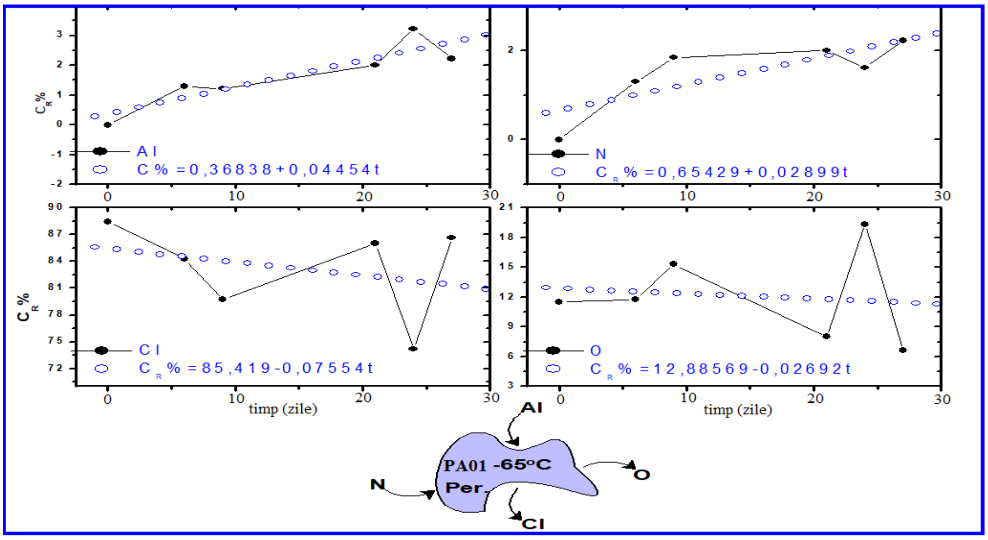

Figure 2: The variation of the content of chemical elements in the structure of the material phase with a majority content of ammonium perchlorate (65°C)

Days of accelerated aging	C_R %						
	Al	**C**	**N**	**Cl**	**Ni**	**Cu**	**O**
0 (Ref.)	0.00	0.00	0.00	88.46	0.00	0.00	11.53
1	1.85	0.00	1.85	79.62	0.00	0.00	16.66
2	4.22	0.00	1.40	81.69	0.00	0.00	12.67
4	1.16	1.16	1.16	80.23	0.00	1.16	15.11
8	2.12	2.12	4.25	61.70	0.00	2.12	8.51
10	3.89	3.89	2.59	61.03	0.00	1.23	27.27

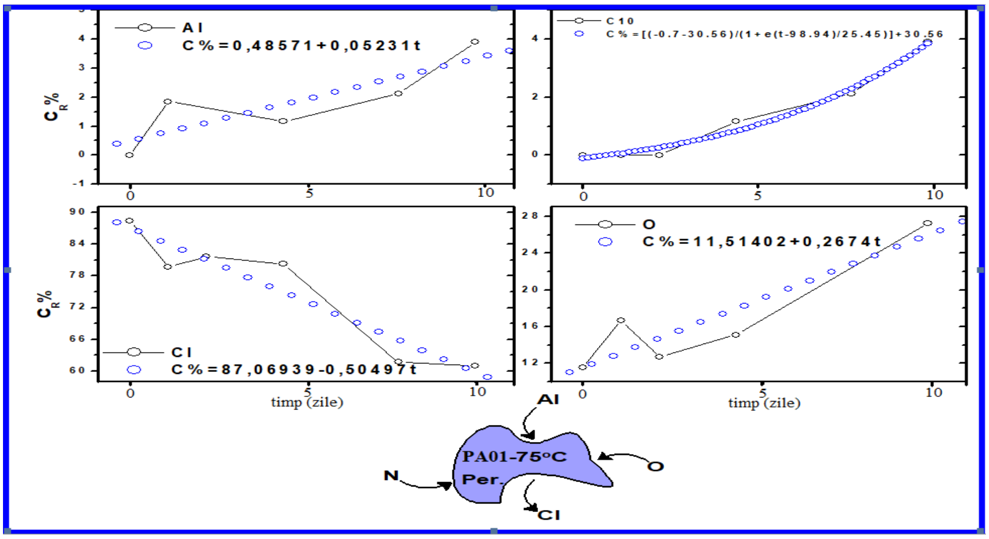

Figure 3: The variation of the content of chemical elements in the structure of the material phase with a majority content of ammonium perchlorate (75°C)

Days of accelerated aging	C_R %						
	Al	**C**	**N**	**Cl**	**Ni**	**Cu**	**O**
0 (Ref.)	0.00	0.00	0.00	88.46	0.00	0.00	11.53
3	1.66	0.00	1.66	85.48	0.00	0.00	11.29
4	1.61	0.00	1.61	85.48	0.00	0.00	11.29
5	1.77	0.00	0.59	72.19	0.59	0.59	13.61
7	1.03	0.00	1.03	82,47	1.03	0.00	14.43
15	1.78	0.00	1.78	83.93	0.00	0.00	12.50

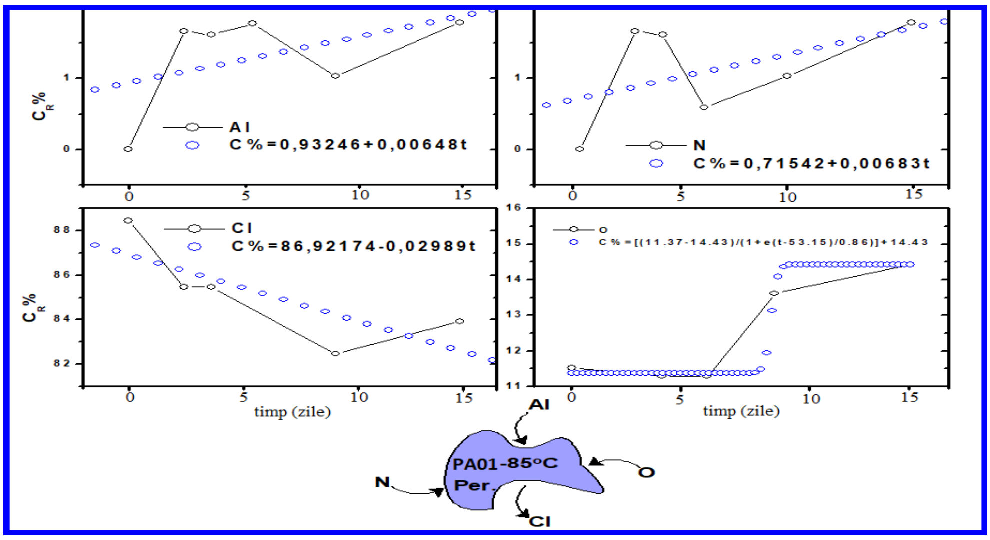

Figure 4: The variation of the content of chemical elements in the structure of the material phase with a majority content of ammonium perchlorate (85°C)

4.2. FTIR/ATR Analysis

Figure 5 shows the IR microspectra for the group corresponding to the $ClO4^-$ anion, wavelength 625.4 cm^{-1} and Figure 6 shows the IR microspectra for the group corresponding to the $NH4^+$ anion, from ammonium perchlorate, wavelength 1427 cm^{-1}, in within the 3 accelerated aging processes, with a temperature contained in the range 65 - 85^{o}C.

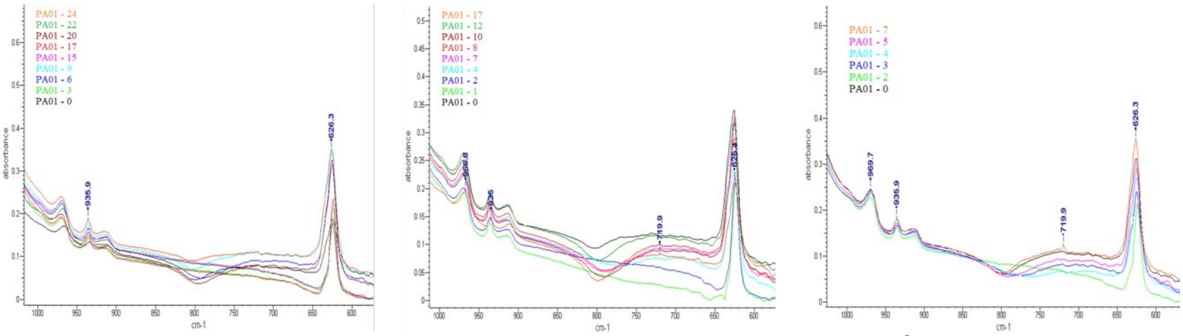

Figure 5: IR microspectra of $ClO4^-$ anion group, wavelength 625.4 cm^{-1}, from ammonium perchlorate, accelerated aging process 65^{o}C (left), 75^{o}C (middle), 85^{o}C (right)

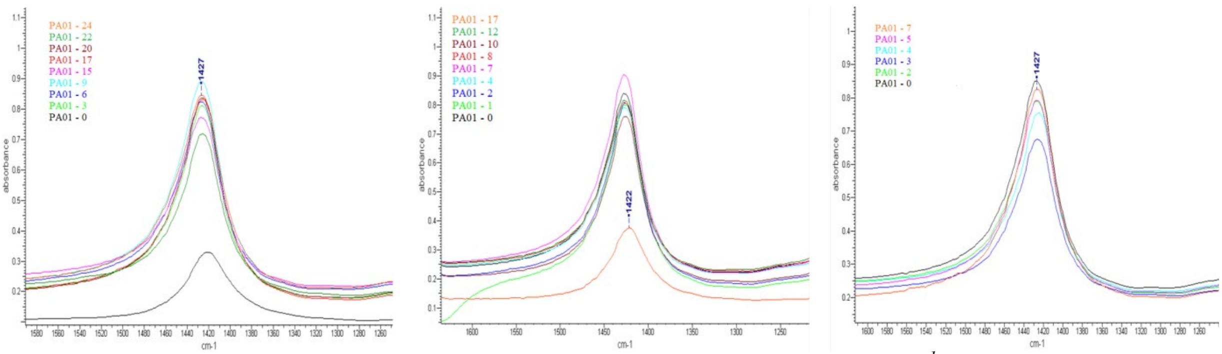

Figure 6: IR microspectra of the NH4+ ion cluster, wavelength 1427 cm^{-1}, from ammonium perchlorate, accelerated aging step 65^{o}C (left), 75^{o}C (middle), 85^{o}C (right)

4.3. Determination of Auto-Initiation Temperature

The explosion (auto-initiation) temperature is defined as the temperature at which a small sample of explosive placed in a test tube and heated externally at a constant rate self-initiates, a phenomenon accompanied by a pop or hiss.

Apparatus: Apparatus for determining the auto-initiation temperature. Operating parameters: temperature range: 30-400°C; heating speed: 0.5-20°C/min.; temperature accuracy: ±0.1°C; the self-starting temperature sensor consists of a temperature controller that allows easy reading of the measured temperatures.

Table 2 shows the comparative results regarding the self-initiation temperature of the composite solid fuel composition analyzed under normal climatic conditions and after completing an accelerated aging program at 65°C for 24 days.

Table 2 Auto-initiation temperature for unaged-aged solid fuel composition

Sample code	**Auto-initiation temperature (°C)**		**Sample code**
Unaged solid fuel composition		Aged solid fuel composition	
PA01$T_0$1N	244.1	248.2	PA01-1Î
PA01$T_0$2N	243.0	247.4	PA01-2Î
Average of measurements	**243.55**	**247.8**	

5. Conclusions

A protocol for accelerated aging and testing of a new solid rocket motor fuel composition was presented by evaluating the behavior of ammonium perchlorate by 2 different techniques, SEM/EDX and FTIR/ATR and determining the auto-initiation temperature. Following the studies carried out: i) no changes in the structure of the aged samples were found, the functional groups corresponding to ammonium perchlorate did not support changes in the IR wavelengths compared to those initially investigated; ii) the fuel tested does not contain microcracks and is not morphologically degraded; iii) the tested samples did not show any reaction (smoke, flame, explosion) at temperatures lower than 80°C.

Through the techniques addressed, it was highlighted that there are no chemical interactions between the components and no phenomena were observed that can modify the aging characteristics of the composite fuel as a whole.

Accelerated aging studies regarding the evaluation of solid fuel behavior by SEM/EDX and FTIR/ATR techniques can be supporting elements in the testing and evaluation of energetic materials during a life cycle, respectively studies for the evaluation of mechanical characteristics, performance and safety characteristics of energetic materials.

Accelerated aging is an indicated and effective form for investigations related to the lifetime of fuels.

Acknowledgements

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References List

[1] T. Rotariu, *Chimia explozivilor*, București, 2010.

[2] Akhtar K., Khan S.A., Khan S.B., Asiri A.M. (2018) *Scanning Electron Microscopy: Principle and Applications in Nanomaterials Characterization*. In: Sharma S. (eds) Handbook of Materials Characterization. Springer, Cham.

[3] Azad MOHAMMED, Avin ABDULLAH, *Scanning Electron Microscopy (SEM): A Review.*

[4] J. Zhi, W. Tian-Fang, L. Shu-Fen, Z. Feng-Qi, L. Zi-Ru, Y. Cui-Mei, L. Yang, L. Shang-Wen and Z. Gang-Zhui, *Thermal Behavior of Ammonium Perchlorate and Metal Powders of different grades*.