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Characterization of New Lead-free Ballistic Modifiers and Phthalate-free Plasticizers in Propellants

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ABSTRACT: This paper describes the synthesis and characterization of a copper-based ballistic modifier, copper subsalicylate (monobasic copper salicylate), and its performance in green-type propellants. New lead-free ballistic modifiers and phthalate-free plasticizers with reduced toxicity, less harmful to the environment, have been employed to replace their traditional additives in green-type double-base propellant preparations. The characterization of the chemical compound was performed by FTIR, TGA-DSC, and WAXS, indicating that copper subsalicylate was obtained. The results of the characterization of propellant compositions showed that copper subsalicylate, in combination with a bismuth salt, could be a substitute for the traditional lead-based ballistic modifier producing green-type propellants without reducing ballistic performance.

KEYWORDS: Double base propellant; Lead-free ballistic modifier; Copper subsalicylate.

INTRODUCTION

The main components of double base (DB) propellants are nitrocellulose (NC) and nitroglycerin (NG). Apart from these components, small quantities of additives that have the function of modifying the mechanical, ballistic, or chemical properties of propellants are incorporated into the formulation (Agrawal 2010).

Ballistic modifiers are added to propellant formulations with the function of controlling its burning rate leading to improved performance and increased ammunition range. Failure to control the burning rate can result in the inadequate performance of a rocket motor propellant or similar. In some cases, the propellant may produce too high or too low operating pressures outside the scope required by the artifact (Neidert and Askins 1994). The traditional ballistic modifiers for rocket engine propellant are lead-based. Lead is a heavy metal known to be harmful to health and the environment due to its toxic and pollutant character. Lead modifiers are generally used in propellants with the inclusion of small amounts of copper in order to increase the propellant burning rate and platonize combustion in certain pressure regions (Agrawal 2010).

Plasticizers, on the other hand, are additives incorporated into double-base propellants to alter properties such as flexibility and durability. Phthalate-based plasticizers are traditionally used, but they are highly toxic and harmful to health, in addition to having been banned from several countries (Neidert and Askins 1994).

New safer and nontoxic chemical additives have been studied in order to replace the additives traditionally used in the double-base propellant compositions, without impairing the propulsion performance of the ammunition or even looking for its improvement.

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Bismuth and copper salts are promising as catalysts for the burning rate of propellants (Agrawal 2010; Zhao *et al.* 2013; Thompson *et al.* 1997; Berteleau *et al.* 1971). In the present work, bismuth- and copper-based modifiers were used to eliminate lead from the composition, as well as a citrate-based plasticizer that is safer for humans and the environment, replacing the phthalate-based plasticizer. For comparison, a ballistic modifier in the form of a complex chemical compound based on lead and copper was also used in propellant compositions containing the traditional phthalate-based plasticizer.

EXPERIMENTAL

The copper subsalicylate compound was synthesized from salicylic acid and basic copper carbonate in an ethyl alcohol solution at 33% w/w, with a molar ratio of 2.2:1. The obtained product was characterized by Fourier transform infrared spectroscopy (FTIR), wide-angle X-ray scattering (WAXS) and thermogravimetric analysis (TGA). Some propellant DB compositions were also prepared using traditional additives and the proposed substitutes (Table 1).

Table 1. DB propellant compositions.

Composition	NC, NG and additives (%)	Complex ballistic modifier PB-Cu (%)	Phthalate-based plasticizer (%)	Citrate-based plasticizer (%)	Bismuth subsalicylate (%)	Copper subsalicylate (%)
A	91.7	4.0	4.3	0.0	0.0	0.0
B	91.7	4.0	0.0	4.3	0.0	0.0
C	91.7	0.0	0.0	4.3	4.0	0.0
D	91.7	0.0	0.0	4.3	2.0	2.0

The traditional ballistic modifier, a complex lead and copper compound were used in compositions A and B, and in compositions C and D, the ballistic modifier was replaced by a bismuth salt (bismuth subsalicylate), together with the chemical compound synthesized with copper. Phthalate-based plasticizer was used in composition A, and citrate-based plasticizer was used in compositions B, C and D. Studies of chemical stability, energy potential, and burning rate of propellant compositions was performed.

RESULTS

The synthesized product presented a dark green color (Satriana, 1971). Figure 1 shows the FTIR spectra of salicylic acid, copper carbonate, and synthesized copper subsalicylate. The enlargement of the absorption of the hydroxyl axial deformation of the phenolic group (3400 to 3000·cm^{-1}) can be observed in the spectrum of the compound, indicating a intermolecular hydrogen bond, the disappearance of the band at 1654 cm^{-1} attributed to the deformation of the C=O bonds of salicylic acid, the appearance of the band at 1600·cm^{-1} attributed to the asymmetric axial deformation of the anion salicylate and the disappearance of the O–H carboxylic acid axial deformation bands (3238 to 2538·cm^{-1}) (Silverstein *et al.* 1979; Kucková *et al.* 2015). This fact may indicate the formation of copper subsalicylate or copper monobasic salicylate.

Thermal analyses showed that salicylic acid is stable up to about 100 °C, when decomposition begins, melting at 158 °C; copper carbonate is stable up to 170 °C. The copper subsalicylate is stable up to 120 °C, and its first weight loss occurs between 120 and 170 °C (7.4% loss). From 260 °C, the DTG curve shows four more decomposition steps, the second weight loss in the range of 270 to 300 °C (3.0% loss), the third and fourth are superimposed between 300 and 350 °C (7.7% loss), and the last weightw loss with 32%, occurs between 360 and 430 °C. The exothermic peak at 430 °C in the last step is attributed to the compound oxidation (Satriana 1971).

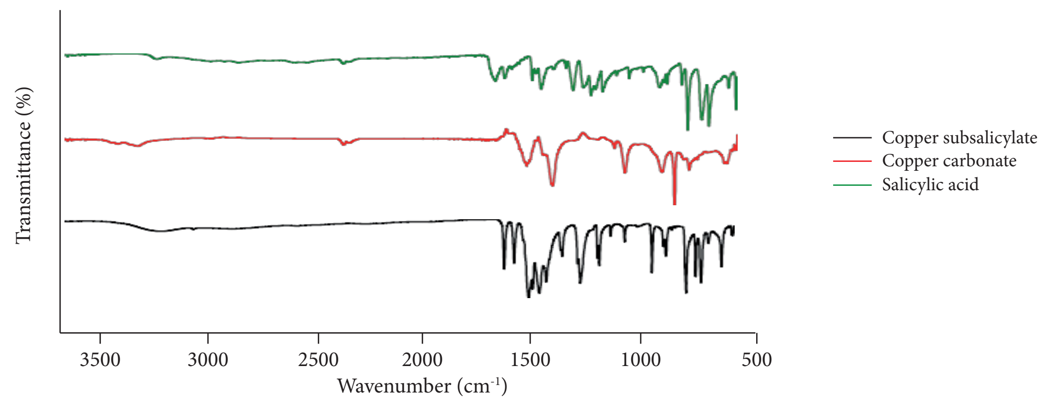

Figure 1. FTIR spectrum.

By WAXS analysis, the main peaks of higher intensity were observed in the following angles 2θ for the synthesized copper subsalicylate: 28.3°; 29.8°; 22.7°; 17.9°; 19.1°; in decreasing order of intensity (Satriana 1971). The main diffraction peaks observed for salicylic acid were: 11.0°; 17.2°; 25.2°, and for copper carbonate were: 31.25°; 32.2°; 35.7°. These peaks were not observed in the diffractogram of the synthesized compound, and it can be concluded that copper subsalicylate was obtained.

The results of the characterizations of DB propellant compositions are presented in Table 2. The replacement of the phthalate-based by the citrate-based plasticizer (composition B) led to a small reduction in energy potential when compared to composition A. The compositions C and D had lower energy potentials than the compositions A and B, which contained lead. All the compositions were approved in the chemical stability tests. Analyzing the linear burning rate under different pressures, the compositions A and B showed higher speed with a tendency to stabilize the pressure. The compositions containing bismuth salt had their linear burning velocities reduced in relation to the values of the compositions A and B. The composition D increased and maintained the burning rate constant in a pressure range in relation to the composition with bismuth salt only. Depending on the requirements of the weaponry, synthesized copper subsalicylate can be used together with bismuth salt as a modifier of ballistic properties.

Table 2. Characterization of propellant compositions.

Composition	Heat of combustion (cal/g)	SD	Chemical stability at 120 °C (min) turning/steam/explosion	Linear burning speed (mm/s)*			
				1100 psi	1300 psi	1500 psi	1700 psi
A	1,179.69	12.23	240/260/>5	19.2 (± 1.2)	19.2 (± 0.6)	19.0 (± 1.8)	15.4 (± 1.0)
B	1,144.75	13.07	250/270/>5	18.3 (± 1.3)	18.7 (± 0.8)	18.1 (± 0.7)	14.1 (± 1.2)
C	1,003.03	36.15	240/260/>5	9.5 (± 0.6)	10.9 (± 0.4)	11.4 (± 0.3)	12.2 (± 0.6)
D	1,098.09	22.32	210/240/>5	13.3 (± 0.0)	15.0 (± 0.7)	15.0 (± 0.4)	16.3 (± 1.0)

*Uncertainty, 90% confidence level; SD: Standard Deviation

CONCLUSIONS

The copper subsalicylate was synthesized and characterized by FTIR, WAXS, and TGA-DSC, indicating its obtention. The results presented indicate the possibility of using the citrate plasticizer in propellant compositions, replacing the traditional phthalate plasticizer, without loss of performance. The evaluation of a composition for use as a propellant depends on several factors, such as energy potential, linear burning rate, mechanical properties, chemical, thermal, and physical stability, besides ballistic properties.

Bismuth and copper-based ballistic modifiers can replace the traditional lead-based ballistic modifiers in propellant compositions, depending on the ballistic assessments to be later conducted and the requirements of the weaponry to be used.

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