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Performance evaluation of commercial copper chromites as burning rate catalyst for solid propellants

Abstract: Copper chromites are well known as burning rate catalysts for the combustion of composite solid propellants, used as a source of energy for rocket propulsion. The propellant burning rate depends upon the catalyst characteristics such as chemical composition and specific surface area. In this work, copper chromite samples from different suppliers were characterized by chemical analysis, FT-IR spectroscopy and by surface area measurement (BET). The samples were then evaluated as burning rate catalyst in a typical composite propellant formulation based on HTPB binder, ammonium perchlorate and aluminum. The obtained surface area values are very close to those informed by the catalyst suppliers. The propellant processing as well as its mechanical properties were not substantially affected by the type of catalyst. Some copper chromite catalysts caused an increase in the propellant burning rate in comparison to the iron oxide catalyst. The results show that in addition to the surface area, other parameters like chemical composition, crystalline structure and the presence of impurities might be affecting the catalyst performance. All evaluated copper chromite samples may be used as burning rate catalyst in composite solid propellant formulations, with slight advantages for the SX14, Cu-0202P and Cu-1800P samples, which led to the highest burning rate propellants.

Keywords: Copper chromite, Composite propellant, BET, Burning rate catalyst.

INTRODUCTION

Composite solid propellants are used as the energy source for the propulsion of solid rocket motors. This kind of propellant is considered a heterogeneous mixture in which solid particles are embedded in a polymeric matrix (binder) (Kubota, 2007; Davenas, 2003; Rezende et al., 2002).

Nowadays, the most commonly used polymer is hydroxyl polybutadiene, which acts as a binder for the solid particles and also as a fuel during the combustion of the propellant. The solid particles are mainly composed of an oxidizer, usually ammonium perchlorate (AP), and a metallic fuel, usually aluminum powder, used to increase the temperature of the combustion products (Prajakta et al., 2006; Ma and Li, 2006; Sciamareli, Takahashi and Teixeira, 2002).

In addition to the basic components, the propellant formulation contains other ingredients like plasticizers, bonding agents and combustion catalysts. The latter have

the function of increasing the burning rate of the propellant (Prajakta et al., 2006; Kubota, 2007; Li, Cheng, 2007).

This happens when one can no longer increase the burning rate through decreasing the particle size of the solid components, for example, the ammonium perchlorate used as oxidizer (Kubota 2007; Prajakta et al., 2006).

The first catalysts evaluated as accelerators for the thermal decomposition of AP based propellants were the transition metal oxides, like ferric oxide (III) (Fe_2O_3), cobalt oxide (III) (Co_2O_3), manganese oxide (MnO_2), chromium oxide (III) (Cr_2O_3) and copper chromite (II) (CuCr_2O_4). The efficiency of these catalysts was also evaluated in the thermal decomposition of AP only (Ma, Li, 2006). The characteristics of the metal oxides, such as particle size, surface area and defects in the crystalline structure may affect the burning behavior of ammonium perchlorate based propellants (Engen and Johannesen, 1990; Ma and Li, 2006).

Different mechanisms have been suggested to explain the thermal decomposition, but no model is completely satisfactory (Kishore and Sunitha, 1979; Carvalheira, Gadiot and Klerk, 1995).

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Among the metal oxides, the most widely used as burning rate catalysts for composite propellants have been iron oxide and copper chromite (Prasad, 2005). The latter has been considered the most effective, due to the spinel shape of its crystalline structure and the arrangement of copper in its structure (Boldyreva *et al.*, 1975).

Pekel *et al.* (1990) studied the effect of two iron oxides with different specific surface area on the burning rate of composite propellant. They observed that the greater the specific surface area the higher the propellant burning rate. A similar conclusion was reached by Burnside (1975) and Engen and Johannessen (1990), on evaluating the effect of the specific surface area and particle size of different types of iron oxide on the burning rate of composite propellants.

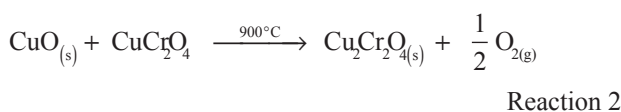
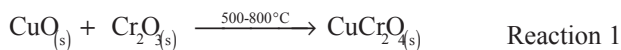
Considering the performance of a rocket motor, it is known that the propellant burning rate varies according to the internal pressure of the combustion chamber (Kubota, 2007; Li and Cheng, 2007) usually expressed by the equation of Saint Robert and Vieille (Eq. 1):

$$V_b = a \cdot P^n \quad (1)$$

Where V_b is the burning rate (mm/s), a is the constant rate, P is the combustion chamber pressure (MPa) and n is the pressure exponent. The latter, with typical values between 0.2 and 0.7, indicates the sensitivity of the burning rate with pressure variation (Davenas, 2003; Benmahamed *et al.*, 2002). Practically, it is desirable that the value of n be as low as possible in order to increase the stability of combustion of the propellant.

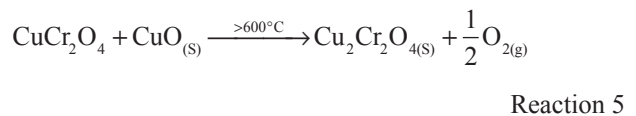
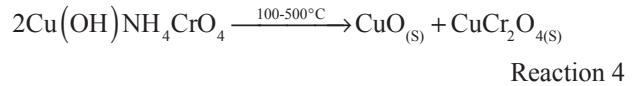
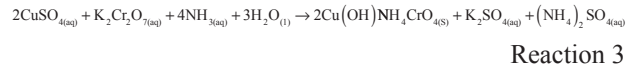
The value of n depends on the composition of the propellant and, mainly, on the characteristics of the burning rate catalysts (Davenas, 2003).

Copper chromite can be synthesized by ceramic method (oxide method), co-precipitation method and also via citric acid synthesis (Li, Cheng, 2007). The ceramic method consists of calcination of copper oxide (II) (CuO) and chromium oxide (III) (Cr₂O₃) mixtures at 500 to 800°C, usually containing stoichiometric amounts of both reactants (Reaction 1). If the calcination is carried out at a higher temperature (900°C), copper chromite (I) (Cu₂Cr₂O₄) will be formed (Reaction 2):



In the co-precipitation method, the catalyst is obtained by calcinations at 100 to 500°C of basic copper chromate

(Reaction 4), which is first obtained from the reaction between potassium dichromate and pentahydrated copper sulfate in the presence of ammonia (Reaction 3). By increasing the calcination temperature to 600°C or higher, copper chromite (I) can be formed (Reaction 5).



Previously, copper chromite was synthesized in our laboratories by the two methods presented above (Kawamoto *et al.*, 2004). Different techniques based on infrared analysis (IR), like transmission, diffuse reflection (DRIFT) and photoacoustic, were used aiming the characterization of the catalysts prepared by the two methods (Campos *et al.*, 2003). It was observed that through the appropriate use of different IR techniques, it is possible to identify the copper chromite synthesis method.

Based on these results, copper chromite samples from different suppliers and synthesis methods were analysed in our laboratories by different IR techniques. With copper chromite samples from the same supplier, it have been observed IR bands related to the reagents used in the synthesis, and the better results have been obtained with the surface analysis techniques (DRIFT and PAS) (Campos *et al.*, 2003).

In this work, copper chromite samples from different suppliers were evaluated as burning rate catalysts in a typical composite propellant formulation. Firstly, the catalysts were analyzed by chemical (Furman, 1996), FT-IR and BET techniques (Campos, 2004). Afterwards, the catalysts were individually incorporated into the propellant formulation for hardness, tensile strength, density and mainly burning rate evaluation. There is an attempt to correlate the characteristics of the catalysts with the propellant properties (Campos, 2004).

EXPERIMENTAL

Copper chromite samples

The following copper chromite samples were evaluated in this work: Cu-0202P, Cu-1950P and Cu-1800P from

Engelhard; HOX 80:20 and HOX 50:50 from Oxiteno; a sample from IPM (Instituto de Pesquisa da Marinha); and SX 14 from AEQ (Aliança Eletroquímica). A sample of iron oxide catalyst (23 FF from Globo) was used for comparison.

Chemical analysis

The copper content of each sample was determined by electrogravimetric analysis and the chromium content was determined by volumetric analysis (Furman, 1962).

Instrumental neutron activation analysis

The copper and chromium contents of each sample were also measured by instrumental neutron activation analysis (INAA), at Instituto de Pesquisas Energéticas e Nucleares (IPEN) and Laboratório de Radioisótopos (Centro de Energia Nuclear na Agricultura of Universidade de São Paulo). The INAA consists in irradiating the samples (50 - 300 mg) with a neutron flux of about $10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ for 1 hour and then measuring the induced radioactivity after 4, 8 and 17 days of radioactive decay, using germanium semiconductor detectors. The neutron flux was estimated by using nickel-chromium wires irradiated together with the samples. The copper/chromium contents were calculated by a specific software (Tagliaferro et al., 2006).

IR analysis

A FT-IR Spectrum 2000 Perkinelmer was used for IR analyses of the catalysts. The spectra were obtained by KBr transmission technique (0.8:400 mg) in the range of $4000\text{-}300 \text{ cm}^{-1}$, with 4 cm^{-1} resolution and gain 1.

Surface area analysis

The values of surface area of the catalysts were obtained by adsorption of N_2 at 77 K, using Accusorb 2100E Micromeritics equipment (Campos, 2004; D-4222-83, 1983).

Evaluation of the catalysts in the propellant formulation

After characterization, 2% (w/w) of each catalyst was incorporated into a typical composite propellant formulation (named PC18) based on HTPB binder (14%), ammonium perchlorate (72%) and aluminum (12%). The propellant formulation was processed in a vertical mixer, under vacuum and at $48 \text{ } 50^\circ\text{C}$. The propellant

viscosity during the mixing process was measured at $48 \text{ } 50^\circ\text{C}$ by a Brookfield viscometer, using a type A spindle at 1 rpm. The propellant cure was followed by shore A hardness measured by a Zwick durometer (NBR 7456). Tensile tests of the propellant samples were carried out in an Instron 1130 machine at room temperature and at 50 mm/s (NBR 9717). The burning rate of the propellant samples was obtained in a Crawford bomb.

RESULTS AND DISCUSSION

IR analysis

According to a previous work (Campos et al., 2003), the KBr transmission IR technique can be used to identify chromite anion bands and also the bands of the raw materials (reagents) used to synthesize the copper chromite by the ceramic or co-precipitation method. The bands at 614 and 524 cm^{-1} , attributed to the Cr_2O_4^- anion, are related to the copper chromite prepared by ceramic method. The bands related to the copper chromite prepared by co-precipitation method are those between $500 - 620 \text{ cm}^{-1}$ (Cr_2O_4^- anion), in addition to those in the range of $1100 - 1200 \text{ cm}^{-1}$ (SO_4^- anion) and those in the range of $800 - 900 \text{ cm}^{-1}$ (CrO_4^- anion) (Miller, Wilkins, 1952).

Figure 1 presents the IR spectra of copper chromite samples evaluated in this work. The spectra A to E indicate that catalysts Cu-0202P, Cu-1950P, Cu-1800P, HOX 80:20 and HOX 50:50, were synthesized by ceramic method. Based on the characteristics bands of the chromite anion, it can be concluded that the IPM and the SX14 copper chromites (spectra F and G) were synthesized by co-precipitation method. In addition, the band at 800 cm^{-1} , which is the main difference between spectra F and G, can be attributed to the reagents used in the synthesis of each copper chromite. According to the literature, solutions of chromium and copper nitrate can also be used as reagents in the co-precipitation method (Carvalho, Feitosa and Rangel, 2000; (Li, Cheng and 2007). As the band close to 800 cm^{-1} is in the region of chromate and nitrate absorptions (Miller, Wilkins, 1952), it can be concluded that the IPM and SX14 copper chromites were synthesized by co-precipitation method. In the case of SX14 copper chromite, this conclusion was confirmed by the supplier.

Chemical analysis

Table 1 presents the Cu/Cr contents of the copper chromite samples measured by electrogravimetric, volumetric and INAA analyses. Except for the lower Cu content of Cu1800P sample determined by analysis, all other Cu and

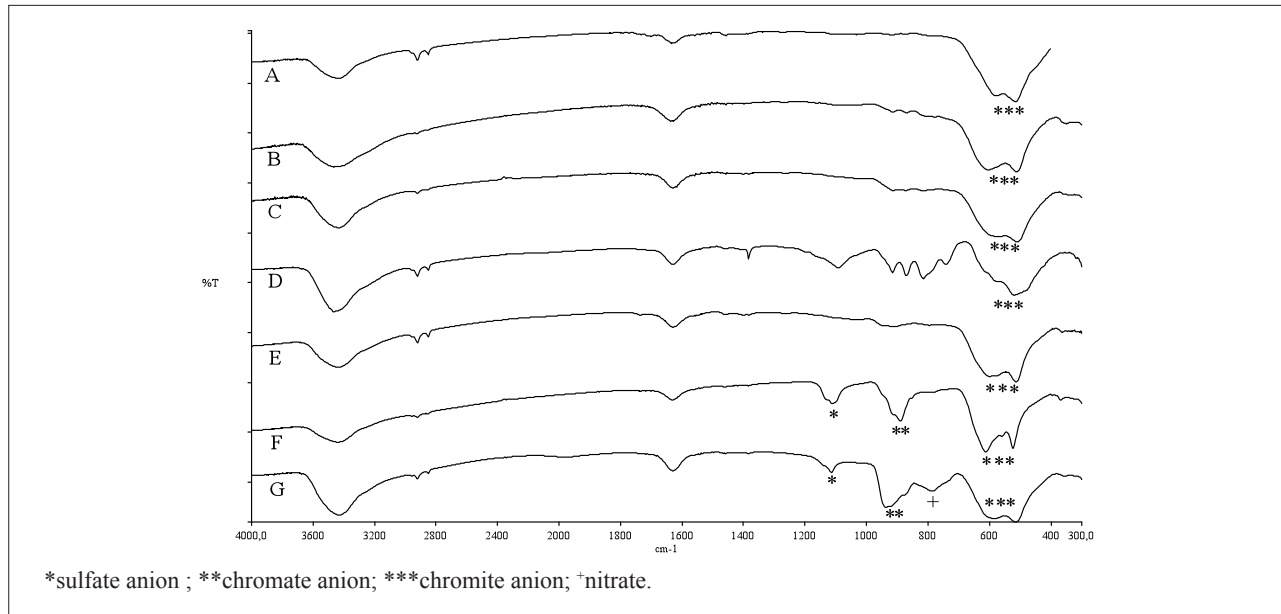


Figure 1: FT-IR spectra - ceramic method: (A) Cu-0202P; (B) Cu-1950P; (C) Cu-1800P; (D) HOX 80:20; (E) HOX 50:50 and coprecipitation: (F) IPM; (G) AEQ SX 14.

Table 1: Cu/Cr contents (w/w) of copper chromite samples measured by electrogravimetric, volumetric and instrumental neutron activation analysis (INAA)

Copper chromite	Electrogravimetric (%Cu)	INAA (%Cu)	Reference (%Cu)	Volumetric (%Cr)	INAA (%Cr)	Reference (%Cr)
SX14	38.4	35.6	-----	25.3	25.5	-----
Cu 0202P	66	63.5	67	10	10	12
Cu 1800P	41.5	38.3	43	30.9	31.3	31
Cu 1950P	36.4	35.7	36	30	32.2	33
HOX 80:20	56.8	58.6	-----	12.1	12.3	-----
IPM	32.7	33.6	-----	28.9	27.8	-----

Cr values determined by the two techniques present good similarity among them.

Surface area

The specific surface area values of the copper chromites evaluated are shown in Table 2, with the properties of the propellant compositions. The catalysts supplied by Oxiteno (HOX 80:20), Engelhard (Cu-1950P and Cu-1800P), AEQ (SX 14), as well as the 23 FF ferric oxide present the highest values of surface area, and the copper chromite from IPM presents the smallest value (3m²/g).

Effect of the catalysts in composite propellant formulation

Table 2 presents the properties of a typical composite propellant formulation containing the different copper

chromite catalysts. The iron oxide containing composition is considered a reference with a burning rate of about 13 mm/s at 6 MPa, measured in a Crawford bomb. The end of mix viscosity (EOM) of each composition is the viscosity value measured just after the incorporation of the curing agent (last component). "Pot life" is the time after the addition of the curing agent, within which the viscosity of the propellant is still suitable (low enough) for casting the rocket motor with the propellant. The values corresponding to "pot life 30 min" and "pot life 60 min" refer to the viscosity of the propellant measured after 30 and 60 minutes, respectively, from the addition of the curing agent.

Concerning the propellant processing, it was observed that the viscosity behavior followed a similar pattern for all compositions, which means requiring three hours of mixing before the addition of the curing agent (data not presented). The lowest EOM viscosity is related to the HOX 80:20 catalyst and the highest values are associated with

Table 2: Properties of a typical composite propellant formulation containing copper chromites from different suppliers

	23FF	Cu-0202P	HOX 80:20	HOX 50:50	IPM	SX 14	Cu-1800P	Cu-1950P
Surface area (m ² /g)	46	19	52	28	3	44	32	34
EOM (Pa.s)	320	312	240	344	376	328	320	400
Pot life 30 min (Pa.s)	408	320	264	360	568	344	344	496
Pot life 60 min (Pa.s)	-----	336	280	384	696	360	360	528
Density (g/cm ³)	1.74±0.01	1.75±0.01	1.75±0.01	1.75±0.01	1.75±0.01	1.75±0.01	1.75±0.01	1.75±0.01
Hardness (Shore A)	72±1	76±1	76±1	77±1	76±1	75±1	74±1	73±1
Tensile strength (MPa)	0.95±0.02	0.90±0.02	0.93±0.02	0.94±0.02	1 ±0.03	1.04±0.01	0.85±0.01	0.85±0.01
Elongation (%)	46±1	38±1	46±2	23±2	36±1	41±2	36±1	49±2
Burning rate equation	6.50.P _c ^{0.41}	7.59.P _c ^{0.36}	5.80.P _c ^{0.45}	6.39.P _c ^{0.42}	5.19.P _c ^{0.46}	6.55.P _c ^{0.47}	6.90.P _c ^{0.43}	5.76.P _c ^{0.40}
Burning rate at 6 MPa (mm/s)	13.4	14.3	13.1	13.5	11.8	15.2	15	11.9

IPM and Cu-1950P catalysts. All other EOM values are not much different from one another, taking into account a typical dispersion of 16 Pa.s for the measures. For most of the compositions, the increase of the pot life viscosity is within the normal range for this kind of propellant formulation. The exception is the highest increase of the pot life viscosity for the composition containing the IPM copper chromite. Even in this case, the viscosity value is still adequate for a good propellant casting.

The density values of the cured propellant compositions are nearly the same, regardless of the copper chromite sample used, and also very similar to the composition with iron oxide. This is an expected result, since the catalyst content (2% w/w) is low compared to the total amount of solids (86%) of the propellant formulation.

Similarly, no remarkable variation was observed in the hardness of the propellant as function of the type of evaluated copper chromite.

In principle, the mechanical properties of the propellant should not be affected by the type of catalyst. In general, the differences observed among the evaluated compositions can be considered normal, taking into account that composite propellants are heterogeneous materials. It can be observed that most of the copper chromite containing compositions present tensile strength (TS) and elongation (ϵ) very close to the composition

with iron oxide. Without any defined reason, the lowest values of TS are presented by the compositions containing the Cu-1800P and Cu-1950P catalysts. Despite this, all TS values can be considered normal, allowing the propellant to be used in a real application. Similarly, the elongation values between 36 and 49% are also considered appropriate for a real application of the propellant. The only value outside this range is the one related to the composition containing the HOX 50:50 catalyst. However, if necessary, this elongation can be increased by adjusting the ratio between the curing agent and the polymeric binder.

Regarding burning behavior, some copper chromites caused an increase in the propellant burning rate in comparison to the iron oxide catalyst. It is observed that the highest burning rate values were obtained with Cu -1800P, Cu -0202P and SX 14 catalysts. In general, the highest burning rate could be associated to the catalysts with the highest specific surface area (Pekel et al., 1990). This assumption is confirmed by the catalyst from IPM, which has the smallest surface area and leads to the lowest burning rate. However, this general rule is not followed by the Cu-0202P catalyst, because despite presenting the lowest surface area it leads to a high burning rate. This behavior could be due to the higher copper content of this catalyst, since it has been suggested that this metal can play an important role in the catalytic activity of copper chromites (Boldyreva et

al., 1975). Generally, it was observed in this work that copper chromites with a copper content higher than 41% lead to burning rates higher than that obtained with the iron oxide catalyst. However, the HOX 80:20 catalyst contradicts the general rules of surface area and copper content. Despite possessing a high surface area and a high copper content, it does not lead, as expected, to the highest burning rate propellant. This has been attributed to any unpredictable experimental mistake.

As previously mentioned, an important parameter related to the combustion of propellants is the pressure exponent (n) of the burning rate equation ($V_b = a \cdot P^n$). Analyzing the data of Table 2, it is observed that for most copper chromites the pressure exponents are close or slightly higher than that related to the iron oxide, with the lowest value being presented by the Cu-0202P catalyst. Despite the small differences, all pressure exponent values enable the propellant to be used in rocket motors for a real application (Kubota, 2007).

With relation to the catalysts evaluated in this work, except SX14, there is no information from the suppliers about the method used to synthesize the catalysts, whether by ceramic or co-precipitation method. For both methods it is known that the formation of the copper chromite takes place when the samples are treated at higher temperatures, being higher in the ceramic method. Carvalho, Feitosa and Rangel (2000) observed that treatments at lower temperatures can increase the specific surface area of the copper chromite. It is believed that different temperatures can lead to the formation of crystals of different shapes and sizes, and this could affect the catalytic activity of the copper chromite (Rajeev et al., 1995; Prasad, 2005).

Some authors evaluated the effect of copper chromite catalysts on the burning behavior of a propellant formulation similar to that used in this work. They observed that the highest burning rates were obtained with the copper chromite obtained by co-precipitation (Faillace, 2001). Using scanning electron microscopy analysis, the increase in the burning rate was attributed to the fact that the copper chromite synthesized by co-precipitation presents larger and better defined crystals than the catalyst obtained by ceramic method. Analyzing the results obtained in this work, it is not possible to identify any effect of the method used to synthesize the catalyst (ceramic or co-precipitation) on the propellant burning rate. The highest burning rate values were obtained with SX 14 and Cu-1800P catalysts, obtained by co-precipitation and ceramic method, respectively.

In conclusion, the results obtained in this work suggest that, in addition to the specific surface area, other characteristics, such as copper and chromium contents, crystalline structure, active surface area (Prasad, 2005) and the presence of impurities, may affect the performance of copper chromites as burning rate catalyst in composite propellants. The possible effect of the active surface area is planned to be evaluated in a future work, by using chemisorption analysis (Webb, 2003).

Despite the inconclusive results, all copper chromites evaluated in this work could be used as a burning catalyst in composite propellant formulations, with slight advantage for the SX 14 sample from AEQ and Cu- 0202P and Cu-1800P samples from Engelhard, which led to the highest burning rates.

CONCLUSION

Copper chromites from different suppliers were characterized and evaluated as burning rate catalysts in a typical composite propellant formulation.

Based on a previous work, the IR analysis allowed identifying the preparation method of each catalyst.

The processing and mechanical properties of the propellant were not significantly affected by the type of copper chromite evaluated, and most of the results are similar to those related to the iron oxide containing composition.

Most of the copper chromites evaluated caused an increase in the propellant burning rate when compared to iron oxide. All copper chromites could be used for a real application of the propellant.

Besides the surface area, other parameters like copper and chromium contents, crystalline structure, active surface area, and the presence of impurities might affect the performance of the catalysts.

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