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Intumescent fire protective coating: Toward a better understanding of their mechanism of action

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Abstract

The aim of this work is to better understand the role and the mechanism of action of boric acid and of coated ammonium polyphosphate (pure ammonium polyphosphate coated with THEIC) used as flame retardants in a commercial intumescent epoxy-based formulation using analytical techniques including thermogravimetric analyses (TGA) and solid-state NMR. In a previous paper, we detected that some reactions took place during the intumescence phenomenon between boric acid and ammonium polyphosphate upon heating. The paper focuses on the analysis of the degradation of those sole components and on the study of their interaction. It is first shown that the THEIC increases the thermal degradation rate of ammonium polyphosphate. This enables the degradation products of boric acid and coated ammonium polyphosphate to react together, resulting in the formation of borophosphate. It is suggested that the formation of this product provides the superior mechanical resistance of the char and promotes the adhesion of char on the steel plate.

Keywords: Intumescence; Ammonium polyphosphate; Boric acid; TGA; Solid-state NMR

1. Introduction

Steel is a material commonly used in the construction of bridges, buildings, boats, cars, and it also plays an important role in other fields like marine or military furniture and offshore platforms. It is a non-combustible material which exhibits a good ductility but it begins to lose its structural properties between 470 and 500 °C [1]. That is because of this low failure temperature that the protection of metallic materials against fire has become an important issue in the construction industry. Indeed, prevention of the structural collapse of the building, which can occur if load bearing steel elements reach a temperature above 550 °C, is paramount to ensuring the safe evacuation of people from the building, and is a prime requirement of building regulations in many countries.

Several means exist for the protection of steel. They are called "passive fireproofing materials", which means insulating systems designed to decrease heat transfer from a fire to the structure being protected. These can be panels or blankets, but usually, coatings such as mineral-based or organic resin-based products, known as "intumescent coatings", are preferred. The use of fire retarded coatings is one of the easiest, one of the oldest and one of the most efficient ways to protect a substrate against fire [2,3]. Indeed, it presents several advantages: it does not modify the intrinsic properties of the material (e.g. the mechanical properties), it is easily processed and may also be used onto several materials including metallic materials [4], polymers [5], textiles [6] and wood [7]. Intumescent coatings are designed to perform under severe conditions and to maintain the steel integrity for one up to three hours when the temperature of the surroundings is in excess of 1100 °C [8–11]. When the temperature of the coating surface reaches a critical temperature under the heat of the flame, the surface begins to melt and is converted into highly viscous liquid. Simultaneously, reactions are initiated that result in the release of inert gases with low thermal conductivity. These gases are trapped inside the viscous fluid (formation of bubbles). The result is the expansion or foaming of the coating, sometimes up to several times its original thickness, to form a protective carbonaceous char (Fig. 1) that acts as an insulative barrier between the fire and the substrate [12].

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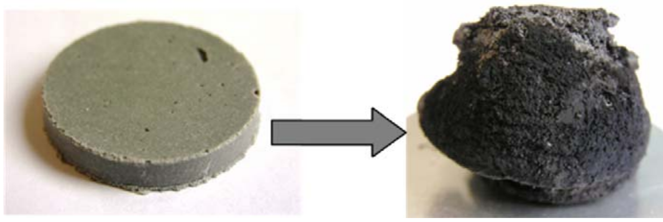

Fig. 1. Swelling of an intumescent coating.

The "intumescence concept" allows a balance between the fire properties and the level of additives in the material. Generally, three intumescent ingredients are used: an acid source, a carbon source and a blowing agent. The formulation of these coatings has to be adapted in terms of their physical and chemical properties to form an efficient protective char.

The mechanism of intumescence is usually described as follows [2,13–15]: first, the acid source breaks down to yield a mineral acid, then it takes part in the dehydration of the carbonization agent to yield the carbon char, and finally the blowing agent decomposes to yield gaseous products. The latter causes the char to swell and hence provides an insulating multi-cellular protective layer. This shield limits at the same time the heat transfer from the heat source to the substrate and the mass transfer from the substrate to the heat source resulting in a conservation of the underlying material.

In intumescent systems, it is essential that the different components incorporated show a suitable matching thermal behavior: a random selection of a component of each of the three classes mentioned above does not ensure intumescent behavior in their mixture. For example, it is obvious that the blowing agent must decompose at a temperature above that at which the charring of the mixture begins, but before the solidification of the liquid charring melt occurs.

In a previous paper [16], it was shown that the combination of ammonium polyphosphate derivative (APP) and boric acid provide an intumescent behavior to an epoxy-based coating. It was observed that their combination inside the resin leads to an important expansion, the formation of a hard char and enables a good adhesion of the char to steel plates, but this interaction has not been further explained. That is why it is essential to study the thermal stability of the different compounds. Thermogravimetric analysis (TGA) will be used in this paper to investigate the thermal stability of the different components as well as the formulation. The potential interactions between the compounds and the reactivity of the system will be also examined. It is expected to get information about the efficiency of the intumescent formulation. This experimental approach will be completed using solid-state NMR to characterize the chemical composition of the intumescent products formed at different characteristic temperatures. The first part of the paper details the analyses of each component and the second part investigates their potential interactions.

2. Experimental

2.1. Materials

Two fire retardant agents were used as received in this study:

- A mineral acid: boric acid (H_3BO_3, purity 95.5%) (Aldrich).
- A commercial ammonium polyphosphate (APP) derivative supplied by Clariant (Germany). It is a blended mixture of ammonium polyphosphate ($(NH_4)_{n+2}P_nO_{3n+1}$) and tris-(2-hydroxyethyl)isocyanurate (THEIC) (Fig. 2).

This compound will be referenced as "coated APP" in the paper.

The ingredients are used separately and then mixed together. Boron is put in excess compared to the phosphorous amount (proportions 1.5 (boron)/1 (phosphorus)).

2.2. Thermogravimetric analysis

Thermogravimetric analyses were carried out at 10 °C/min under synthetic air (flow rate: 50 mL/min, air liquide grade), using a Setaram TG 92 microbalance. The samples (approximately 10 mg) in powder form were placed in open vitreous silica pans. The precision of the temperature measurements was 1.5 °C over the whole range of temperature (20–800 °C). In order to determine whether a potential increase or decrease in the thermal stability happens between two additives mixed together, the weight difference curves between experimental and calculated TG curves were computed as follows [11]:

- $M_{add1}(T)$: values of weight given by the TG curve of the first additive (e.g. boric acid).
- $M_{add2}(T)$: values of weight given by the TG curve of the other additives (e.g. coated APP).
- $M_{exp}(T)$: values of weight given by the TG curve of the mixture (add1 + add2 that is to say e.g. boric acid + coated APP).
- $M_{th}(T)$: theoretical TG curve computed by linear combination between the values of weight given by the TG curve of both additives: $M_{th}(T) = xM_{add1}(T) + (1 - x)M_{add2}(T)$, where x is the "add1" (e.g. boric acid) content of the mixture.
- $\Delta(T)$: weight difference curve: $\Delta(T) = M_{exp}(T) - M_{the}(T)$.

The $\Delta(T)$ curves allow us to show a potential increase or decrease in the thermal stability of the system when two additives are mixed together.

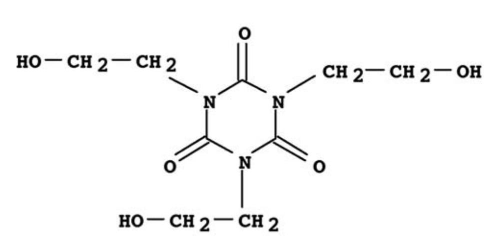

Fig. 2. Formula of THEIC.