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Interactions between chlorinated paraffins and melamine in intumescent paint—investing a way to suppress chlorinated paraffins from the formulations

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Abstract

It is known that acid source, carbon source and blowing agent are the main ingredients of an intumescent paint. Melamine and halogenated additives, such as polychlorinated alkanes (PCAs) are used as blowing agents, however, the legislation tends to prohibit the use of halogenated coumpounds for environmental reasons. The aim of our study is to investigate the mode of action of melamine and PCAs in an intumescent formulation. Their interactions are also studied. It is found that the combination of PCAs and melamine leads to more efficient systems. Spectroscopic analyses (FTIR and solid state ^{13}C NMR) led us to conclude that when the intumescent paint was heated melamine condensed to create melem via Diels-Alder-type reaction. Melem could then react with PCAs leading to the stabilisation of the PCA-melamine mixture. The proposed mechanism of action led us to propose a method for the substitution of PCAs.

Keywords: Intumescence; Melamine; Polychlorinated alkanes; Thermal stability; Fire protection

1. Introduction

The use of fire retardant coatings is one of the easiest, one of the oldest and one of the most efficient ways to protect materials against fire [1,2]. Indeed, it presents several advantages: it does not modify the intrinsic properties of the materials (for example the mechanical properties), it is easily processed and it may be used onto several materials, such as metallic materials [3], polymers [4,5], textiles [6] and wood [7]. Moreover, since ignition occurs usually on the surface of a material it is important to concentrate the protective action at this place.

The protection of metallic materials against fire has become an important issue in the building industry. Indeed, in the case of fire such materials distort leading to the destruction of building structures and as a consequence to dramatic human and economical losses.

Intumescent paints are a way to achieve such a protection. Fire retardant coatings, acting by the phenomena of intumescence, form on heating an expanded multicellular layer, which acts as thermal barrier [8,9]. It prevents heat from penetrating and flames from spreading. As a consequence, this insulative barrier makes intumescent coatings particularly suitable for the protection of structural steelwork.

The intumescent process is a complexe phenomenon that involves chemical and physical processes. It consists of a combination of carbonization and blowing. The chemical reactions between the components of an intumescent system (in particular between the acid source and the carbon source) lead to the formation of a thermally stable material that protects the underlying substrat.

Dry films of intumescent paints, submitted to flame action, soften in a first stage and then swell due to the release of volatile

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[1] Eliokem Materials and Concept is the former Specialty Chemicals Business of the Goodyear Tire and Rubber Cie, proposing a large range of resins for the Coatings Industry.

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degradation compounds reaching up to 200 times their original thickness. The charred coat (usually called char), an incombustible spongy mass, protects the painted material, delays the temperature increase and avoids the access of air, and so the combustion. By means of intumescent coatings, different materials, such as paper, wood, pasteboard, plastics, metals, etc. can be protected. The formulation of the coating has to be optimised in terms of physical and chemical properties in order to form an effective protective char [10].

An intumescent formulation should combine:

- an acid source, such as ammonium polyphosphate
- a source of carbon, such as a polyhydric compound
- a swelling agent, such as melamine. Halogenated additives are also used, however, the legislation tends to prohibit them for environmental reasons.

Halogenated fire retardants, such as chlorinated paraffin decompose to release halogen to terminate fire. Chlorinated paraffins are one of the lowest cost flame-retardants available. Solid chlorinated paraffins have been used to flame retard many polymers, but some applications were limited due to the thermal stability of the chlorinated paraffin and to environmental problems [11]. Chlorinated paraffins or polychlorinated *n*-alkanes (PCAs), in most cases, contain 10–30 carbon atoms and a chlorine content of 30–70 wt.%. They are also used as lubricating oil additives or secondary plasticizers [12]. Chlorinated paraffins are used in intumescent paints since several decades [13,14]. However, even if the patented litterature is important, there are only few paper dealing with their role and effects on the development of the intumescence [15].

The aim of our study is to investigate the role of melamine and PCA in an intumescent formulation and to study their interactions in order to propose a way to substitute PCAs by another component that would not raise environemental hazard. In a first part, the fire protection of several intumescent formulations is evaluated. Then, the thermal stability of the intumescent paints as well as the one of its separate components (melamine, PCA and their mixture) is discussed.

2. Experimental

2.1. Materials

The suppliers of the components used to formulate the intumescent paint are reported in Table 1. The mixture of the components was processed using the following method. First, TiO_2 and ammonium polyphosphate (APP) were dispersed in water. Then, the melamine and the PCA were added into the suspension. Finally, dipentaerythritol (DiPER) and the polystyrene acrylate resin were added to the mixture. The formulations were prepared by mixing the components using an Ultra Turax mixer (600 rpm).

Table 1
Suppliers of the components used to formulate the intumescent paints

Component	Supplier
Polystyrene acrylate resin (water-based emulsion)	Eliokem
Dipentaerythritol (DiPER)	Aldrich
Ammonium polyphosphate (Exolit AP422)	Clariant
TiO_2	Hunstman
Cereclor70 (PCA)	Cereclor
Melamine (MEL)	Aldrich

2.2. Fire protection

Intumescent paints were applied onto the surface of a metallic plate (10 cm × 10 cm − thickness = 3 mm). Thick films of about 2 mm were obtained by deposition of 1200 g/m^2 of intumescent paint.

Temperature profiles were measured at the interface between the intumescent coating and the metallic plate for a sample exposed to a constant heat flux of 35 kW/m^2 under the conditions of the cone calorimeter presented in Fig. 1. A thermocouple is placed in a groove on the back side of the metallic plate and allows the recording of the temperature during the experiment and the drawing of time temperature curves.

2.3. Thermo-gravimetric analysis

Thermo-gravimetric (TG) analyses were carried out at 10 °C/min under synthetic air (flow rate: 50 ml/min, Air Liquid grade) using a Setaram MTB 10-8 microbalance. The samples (about 10 mg) in the form of powder were placed in open vitreous silica pans. The precision of the temperature measurements was 1.5 °C over the whole range of temperatures (20–800 °C).

In order to determine whether a potential increase or decrease in the thermal stability of the paint is related to the presence of a component, the difference weight loss curve ($\Delta(T)$) between experimental and theoretical TG curves were computed as follows:

$\Delta(T) = M_{\text{exp}}(T) - M_{\text{the}}(T)$ where

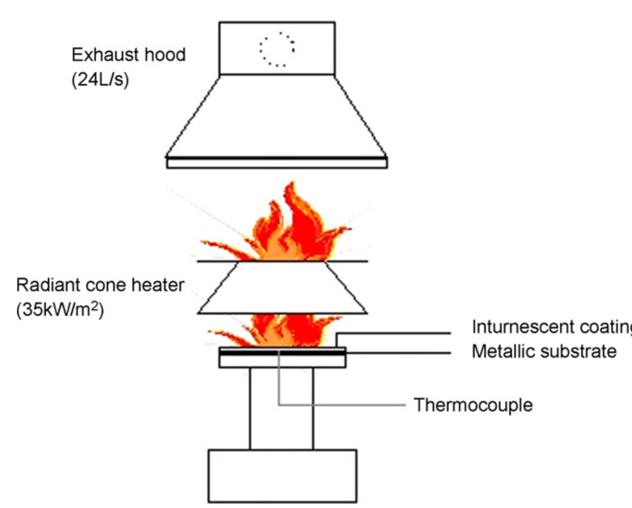

Fig. 1. Experimental set-up of temperature profiles measurements.