The effect of nanosilica on the intumescent fire-retardant coating's properties
(*Rapid communication*)

Kajetan Pyrzyński[1), *)]

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Abstract: The effect of nanosilica on the intumescent fire-retardant coating's properties. Cone calorimetry and a single burning item test were used to determine flammability. The nanosilica-modified intumescent coating allows obtaining a Bs1d0 class non-flammable material for the protection of wood and wood-based materials (e.g., plywood, chipboard, fiberboard, other lignocellulosic composites).

Keywords: flame retardants, intumescent coatings.

Wpływ krzemionki na właściwości pęczniejących powłok ogniochronnych

Streszczenie: Zbadano wpływ krzemionki na właściwości pęczniejących powłok ognioochronnych. Do określenia palności zastosowano kalorymetrię stożkową i test pojedynczego płonącego przedmiotu. Modyfikowana krzemionką powłoka pęczniejąca umożliwia uzyskanie materiału niepalnego klasy Bs1d0 do ochrony drewna i materiałów drewnopochodnych (np. sklejka, płyta wiórowa, płyta pilśniowa, inne kompozyty lignocelulozowe).

Słowa kluczowe: środki zmniejszające palność, powłoki pęczniejące.

Most of the materials around us are flammable – they ignite easily and spread flames quickly, causing dangerous fires resulting in huge material losses and fatalities. Protecting flammable materials from fire is essential. This is due to the need to protect health and life, as well as for economic reasons [1].

One of the most effective methods of flame and fire retardation of combustible materials is the application of intumescent coatings, usually thin layers. The coating can be applied to various substrates, such as polymeric materials, textiles, wood [2], and metals. They are the preferred choice for passive fire protection because they offer aesthetic appearance, flexibility, quick application, and ease of inspection and maintenance [3].

Intumescent flame-retardant coatings have been in use for about 50 years, while the addition of intumescent additives to polymeric materials is a recent approval.

The effectiveness of the protection depends on the quality of the coating, its thickness, and the correct method of application. A particularly important element of good protection of the material is the creation of a compact, uniform, and impermeable protective layer. There is one more important condition – strong bonding of the layer with the protected material. Therefore, the surface of the protected material should be as clean as possible [4].

Some intumescent coatings are designed for use on exposed interior steelwork where a paint-like finish is desired. Others are designed to protect wooden components and other lignocellulosic products, as well as textiles, indoors. They are used in many public buildings, such as offices, healthcare facilities, hotels, restaurants, schools, historic buildings, as well as housing.

Thin-layer intumescent coatings for interiors can be made based on poly(amino silicates), vinyl acetate, or water-soluble silicates (Na^+, K^+, Li^+) and offering a paint-like finish. On the other hand, intumescent coatings used outdoors are most often based on epoxy resins and provide good corrosion resistance. They are used e.g., in the petrochemical industry in refineries and offshore platforms. Due to their high impact strength, adhesion, and moisture resistance, they are also desirable for some indoor applications such as swimming pools and clean rooms. Intumescent epoxy coatings typically require a thick layer (2.5 to 12 mm) and reinforcement with fabric or steel mesh. They are usually applied by licensed applicators and have a more textured surface than thin layers [5].

Intumescent systems (paints, varnishes, sealants, and floor coverings) when heated to high temperatures, form large amounts of non-combustible residues. Under the influence of emitted gases, these substances create foam with good insulating properties. When exposed to heat,

1) Innovative and Implementation Company (PIW) Delta, ul. Krupczyn 5, 63-140 Dolsk, Poland.
*) Author for correspondence: kajetan@melpin.pl

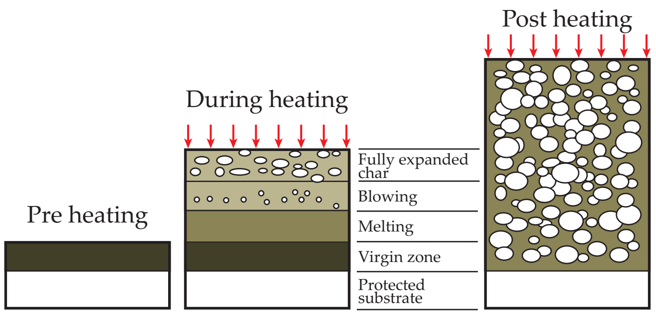

Fig. 1. Schematic illustrations of intumescent coating action [6]

intumescent coatings expand their volume up to 20 times, and even over 200 times.

In the first stage, the dehydrating agent is decomposed, and its ammonium salt, amine, or ester is converted into an acid which reacts with the hydroxyl groups of the carbonizing substance (esterification) to form a thermally unstable ester in the presence of a catalyst. This is followed by a further increase in the decomposition temperature of the ester with the formation of carbon, free acid, water, and carbon dioxide. The free acid reacts again with the hydroxyl groups of the carbonizing substance. The decomposition of the ester is accompanied by the decomposition of blowing agents, resulting in the release of significant amounts of non-combustible gases, which cause swelling of the carbon material (residue of ester decomposition) or silicate (Na^+, K^+, Li^+). A thick, porous layer is formed insulating the combustible material from heat and oxygen and protecting the material from fire. The particularly good thermal protective properties of foamed char and its low weight are the main aspect of the high efficiency of expanding flame retardants. The swelling process is illustrated in Figure 1.

The tendency of the polymer to carbonization can be increased by chemical additives and by changing its molecular structure. For example, some polymer additives, such as poly(vinyl alcohol), promote the formation of charred layers. These additives usually form a highly coupled system in which the aromatic structures carbonizing during thermal degradation have the same temperature near the polymer surface, while the upper surface exposed to flames can be heated up to 1500°C. Therefore, the chemistry of flame retardants is related to carbonization at temperatures from 300°C to 1500°C. Proper selection of intumescent system components have a significant impact on the rate of formation of the carbon or silicate layer, its structure, resistance to thermal factors, durability of the system during storage, and the quality of the coating during its application. Intumescent agents effectively protect both wooden products and steel surfaces against high temperatures [7]. Passive intumescent systems are also advantageous because, unlike water, they do not have the ability to intensify fire.

This is of particular importance in the protection of building structures. By creating a thick carbon layer, intumescent agents protect the structures against high temperature for a relatively short time, but long enough to safely evacuate people from the building. In the case of protecting wood and wood-based surfaces with intumescent paints, a thick, charred porous layer formed under the influence of flame effectively protects the wood against pyrolysis and burning.

The required fire resistance class of building elements can be achieved in many ways, but the use of flame-retardant paints, although not a cheap solution, is extremely aesthetic and allows for obtaining a high-quality surface.

Fire-resistant paint products must meet stringent requirements, such as no harm to humans and animals, both during normal use and in fire conditions, not changing the color of the protected material, not impairing the mechanical properties of wood and composites, and maintaining protective properties for at least three years.

Several types of fire protection paint systems are available on the market, adapted to specific conditions. When choosing a system to protect the structure, attention should be paid to the factors affecting the durability of the coating and its proper functioning. Table 1 shows examples of commercial intumescent coatings.

In Poland, most paints available on the market are imported or produced under foreign licenses. The world's leading manufacturers of intumescent products include Zeroflame (UK), RPM International Inc. (USA), Jotun (Norway), Bollom (UK), Akzo Nobel (The Netherlands), Thermoguard (UK), and Sherwin-Williams (USA).

Current trends in the production and application of intumescent coatings

The aim of the current research on intumescent preparations is to give polymers and polymer composites fire-resistant properties. The use of novel intumescent coatings applied to fabrics, films, and foams by layer-by-layer assembly is nothing new, but when used to impart flame-retardant properties to polymers, it is the latest development.

Innovative systems are mostly based on nanotechnology, synergistic effects, as well as chemical compounds with high endothermic abilities. It was found that nanoadditives such as montmorillonite, hectorite, saponite, two-layer magnesium and aluminum hydroxides improve the fire-retardant properties of intumescent coatings. On the other hand, carbon nanotubes, fullerenes, silica, aluminum, and titanium nanoparticles, as well as silsesquioxanes have a synergistic effect [6]. Hybrid systems in intumescent coatings are also used. For example, soluble organic phosphorus compounds associated with inorganic phosphorus-based systems are used in textile applications [16]. Hybrid intumescent coatings are also used to protect wood against fire [17].

Ammonium polyphosphate (APP) treated zeolite showed excellent fire resistance, heat release rate (HRR), total heat release (THR), smoke rate (SPR), total smoke release (TSR), and fire growth index (FGI) for sawdust board (SB) compared to APP used alone [20].

T a b l e 1. The commercial intumescent fire retardants

Product name	Specification	Producer
UNIEPAL–DREW Aqua Colour	Water-borne impregnation varnish for decorative finishing and fire protection of wooden surfaces.	PPH ADW Ltd, Poland
STEELGUARD	One-component, solvent-based, thin-coat intumescent paint for fire protection of structural steel.	PPG Industries, USA
Sika® Pyroplast® Wood	Water-based transparent coating system for wood fire protection, interior use.	Sika Deutschland GmbH, Germany
MCR Polylack	Paint forming an intumescent fireproof coating.	Mercor Dunamenti Zrt., Hungary
Flame Stal® FireProof Solvent	One-component, thixotropic mixture based on organic solvents. The coating is intended for fire protection of steel and galvanized steel structures made of open and closed profiles. Fire protection elements can be used inside and outside buildings.	Pirosystem Ltd, Poland
Charflame	The purpose of this coating is to maintain the fire resistance and load-bearing capacity of steel structures until the fire is extinguished or the building is evacuated. As a water-based coating, it has a short drying time. Airless spray is the recommended method of application, although a brush or roller may also be used for small areas or repairs.	FIRELANZ, S.L.U., Spain
Fontefire ST60	One-component, water-borne, thin film intumescent coating for efficient fire protection of steel.	Tikkurila, Finland
Hempacore AQ	One-component, water-borne, chlorine-free, physically drying intumescent coating for passive fire protection of structural steel.	Hempel, Denmark
Thermoguard Fire Varnish 30- & 60-Minute System	Clear intumescent varnish for interior and exterior wooden surfaces. The system includes a basecoat and a topcoat [8].	Thermoguard Ltd., UK
FX-100™	Clear two- component, intumescent coating with a significantly lower activation temperature than other intumescent coatings, making it suitable for use on low flash point substrates including wood and some plastics [9].	Flame Seal Products Inc., USA
Hensotherm 310 KS	Solvent-borne intumescent coating for steel protection suitable for outdoor use.	Tecnos, Finland
Sika® Unitherm®	Solvent-free, ultra-high build, two-pack, modified epoxy based intumescent fire protection coating for structural steel.	Sika Ltd., UK
Firefilm FC2	Intumescent coating for fire protection of steel structures.	Carboline, USA
Nullifire SC803	Intumescent coating for fire protection of steel structures; one-coat, low VOC, high-build, fast-curing.	Tremco CPD Ltd., UK
Firetex FX1003	Single component, solvent-based, thin-film intumescent coating designed for on-site and off-site application to provide fire protection to steel structures [10].	Sherwin-Williams, USA
Expander FR	Intumescent system based on urea formaldehyde resins and modifying agents for wood and composites.	PIW Delta, Poland

Hybrid intumescent coatings based on epoxy resins, unlike typical solvent-based or water-based intumescent coatings, not only provide effective fire protection for substrates but are also resistant to moisture and weather conditions [18]. They can be used in outdoor applications, e.g., for passive fire protection of steel structures. An example of this type of coating is hybrid intumescent coatings based on silicone-epoxy resin (with amino silane hardener) [19].

Although the basic concepts of swelling related to chemical composition, temperature, and rheology are well known, the modeling and simulation of these systems are completely new and have never been sufficiently tested [21].

Fig. 2. The condensation apparatus

Current trends in intumescent coatings are the development of epoxy-based and high-solids coatings with lower thickness and shorter drying times for use in harsh environments. Manufacturers are also focusing on more environmentally friendly products and processes, increasing efficiency, and expanding the portfolio to further increase their competitive advantage.

The fireproofing approach based on intumescent systems is widely developed because it has desirable environmental properties.

The aim of the research was to increase the swelling capacity in fire conditions of commercial protective coatings [14]. Flammability was evaluated by cone calorimetry. The coating, filled with nanofillers and other modifiers, is an inexpensive protective layer for wood, lignocellulosic composites, as well as textile materials, it can also be used as a sealing coating and fire barrier in outdoor applications.

EXPERIMENTAL PART

Materials

Urea and melamine, diamide dicyanate, formaldehyde, phosphoric acid or its derivatives containing nitrogen, starch, methoxylated and butoxylate urea-melamine-formaldehyde resin were provided by Grupa Azoty SA (Poland), Brenntag Polska Ltd (Poland), Lerg SA (Poland), Centro-chem Ltd (Poland), Standard Ltd (Poland), and PIW Delta (Poland), respectively. All materials were used in technical grade. Hydrophilic fumed nanosilica (SiO_2) with a specific surface area of 200 m^2/g, purity of 99,8 % and average primary particle seize 12 nm (Aerosil 200) was supplied by Evonik (Germany). The nanosilica was used as a nanofiller in an amount of 1.5 wt%.

Protective coating preparation and testing

Urea or melamine, diamine dicyanate, ammonium phosphate, starch, formaldehyde, and water were added to the reactor equipped with a cooling system (with continuous stirring) (Fig. 2). The mixture was heated to 70°C for 15 minutes, then the temperature was raised to 95°C and condensation continued for another 30 minutes. Then melamine-formaldehyde resin and nanosilica in solid form was added [14].

To determine fire resistance, the obtained material was applied with a roller to the surface of a chipboard (350 g/m^2). The system was mixed thoroughly without dilution before use. After applying the second layer (24 h after the first one) and its complete drying (24 h), nitrocellulose varnish (Capon) was applied in an amount not

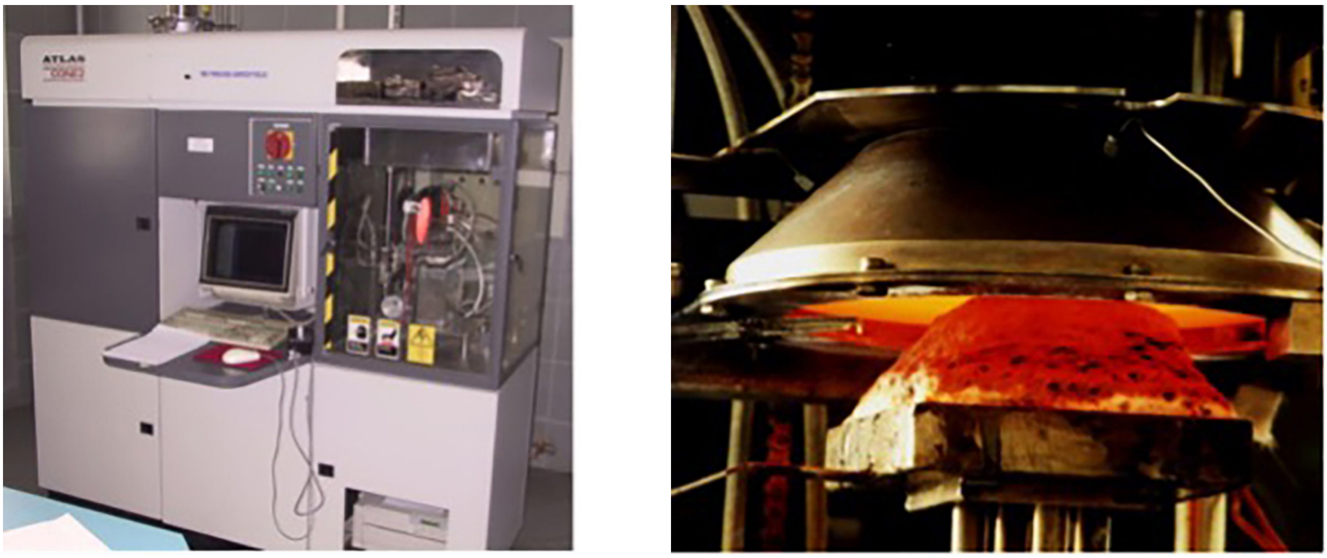

Fig. 3. Cone calorimeter apparatus

T a b l e 2. SBI ignition tests of chipboard covered with the silica-modified intumescent system

Class	Parameter	Results	Requirements
B	$FIGRA_{0.2MJ}$	20.8 W/s	< 120 W/s
	$FIGRA_{0.4MJ}$	20.8 W/s	
	THR_{600s}	2.9 MJ/m^2	
s1	SMOGRA	1.9 m^2/s^2	< 30 m^2/s^2
	$TSP_{600\,s}$	30.4 m^2	< 50 m^2
d0		No flaming droplets or particles	No flaming droplets or particles

T a b l e 3. Fire retardant performance of the silica-modified intumescent system

Kind of materials	Fire retardant ground coat g/m^2	Surface varnish g/m^2	Classification acc. to PN-EN1 15101-1+A1
Pine wood one side protected	350	80 – 100	Non-flammable Bs1d0
Chipboard with natural veneer one side protected	350	80 – 100	Non-flammable Bs1d0
Plywood one side protected	350	80 – 100	Non-flammable Bs1d0
Fiberboard soft – hard one side protected	350	80 – 100	Non-flammable Bs1d0

exceeding 110 g/m^2, in accordance with the user manual. The product without and with the addition of nanosilica was tested. A reference sample without fire retardant coating was also tested.

Methods

Cone calorimetry

Combustibility assessments were carried out on the CONE2A cone calorimeter made by Atlas Electric Devices Co., USA (Fig. 3). Measurements were carried out in accordance with ISO 5660-1. The samples (10 × 10 cm) were exposed to an external heat flux of 50 kW/m^2. The orientation of the sample was horizontal, and a spark igniter was used to ignite the combustion gases. The heat release rate (HRR) as a function of time, maximum and average heat release rate (HRR_{max}, HRR_{av}), time to reach HRR_{max}, total heat release (THR) and time to sustained ignition (TTI) were recorded.

Single burning item test (SBI)

The SBI test simulating the burning of a single object in the corner of the room was performed in accordance with the PN-EN 13823 standard (Fig. 4).

Fig. 4. The single burning item test

The total exposed area of the sample was 1.5 × 1.5 m. The specimen consisted of two pieces forming a rectangular corner. A 30-kW propane diffusion triangular gas burner acted as a source of heat and ignition, resembling a burning wastebasket. Based on the recorded data, the values of the main classification parameters were determined: fire growth rate indicator (FIGRA), total heat released and total smoke emission from the sample during the first 600 s of exposure to the flames of the main burner (THR600s and TSP600s, respectively), as well as smoke emission rate indicator (SMOGRA).

RESULTS AND DISCUSSION

The effect of nanosilica on the combustion parameters obtained from the cone calorimetry is shown in Fig. 5. Nanosilica significantly extended the time to ignition and shortened the time to reach the HRR peak. Moreover, the rate of heat release increased. The total heat release rate was comparable to that without silica. The tested product formed an intumescent charred coating during the cone calorimetry test (Fig. 6), effectively protecting the materials against thermal decomposition [11].

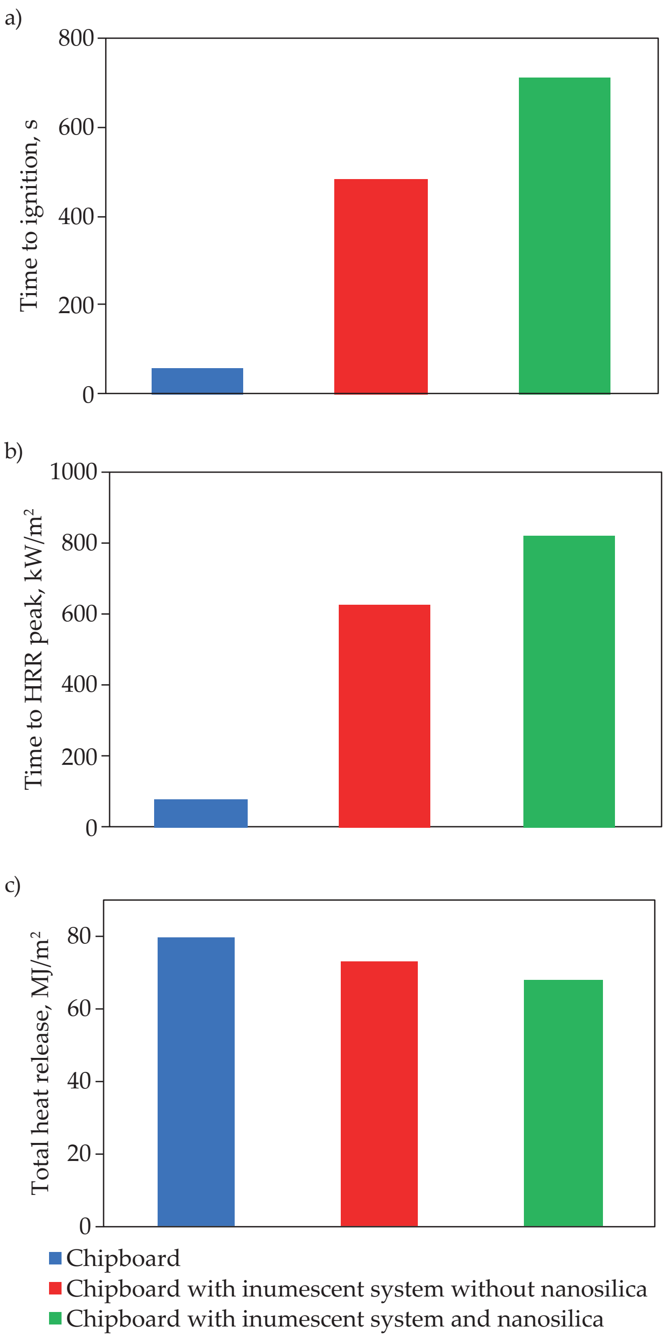

Fig. 5. The effect of nanosilica on the combustion parameters

There is a strong correlation between charring efficiency and fire resistance because charring occurs at the expense of combustible gases and the presence of char inhibits the spread of flames by acting as a thermal barrier around unburnt material. Protecting the material against excessive temperature increases and oxygen penetration limits its thermal decomposition and, consequently, the loss of mechanical properties.

The fire-retardant effectiveness of the modified varnish was also confirmed by the results of the SBI ignition test of a chipboard covered with the developed intumescent system and Capon nitrocellulose varnish (Table 2) [12].

Fig. 6. Ceramic surface with intumescent coating

Based on the recorded data and the requirements of the PN-EN 13501-1 standard, reaction to fire classes A2, B, C or D were determined. Table 2 shows that the FIGRA, THR, SMOGRA and TSP parameters were lower than required. No falling parts or drops were observed [12]. These results qualify the modified intumescent coating as a non-flammable material of Bs1d0 class for protecting wood and wood-based materials, such as plywood, chipboard, fiberboard, and other lignocellulosic composites in an amount of 350 g/m^2 (Table 3) [13].

The tested product does not change the natural appearance of the protected material due to the transparency of the coating. To protect against moisture, the coating of the product requires the application of a surface varnish. In addition, the product has been tested as safe for the environment and human health, non-toxic, based on waste-free technologies and obtained the Hygienic Certificate of the National Institute of Hygiene and the National Technical Assessment in Poland [15]. Such materials will be used wherever, in addition to high fire protection efficiency, a decorative appearance of the materials used is necessary, e.g., in construction. The varnish is not recommended for the protection of surfaces exposed to heavy mechanical loads (e.g., doors, furniture, wooden floors).

CONCLUSIONS

Nanosilica has been used to increase the swelling capacity of commercially available protective coatings under fire conditions. Nanosilica significantly extended the time to ignition and shortened the time to reach the HRR peak. Moreover, the rate of heat release increased. The total heat release rate was comparable to the heat release rate for the coating without silica. The resulting swelling charred coating effectively protected the material against thermal decomposition. FIGRA, THR, SMOGRA and TSP parameters were lower than required. No falling particles or drops were observed. For the protection of wood and wood-based materials, such as plywood, chipboard, fiberboard and other lignocellulosic composites, a non-flammable Bs1d0 class material in the amount of 350 g/m^2 was obtained.

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