Silicone Resin-Based Intumescent Paints

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Silicone resins are widely applied as coating materials due to their unique properties, especially those related to very good heat resistance. The most important effect on the long-term heat resistance of the coating is connected with the type of resin. Moreover, this structure is stabilized by a chemical reaction between the hydroxyl groups from the organoclay and the silicone resin. The novel trends in application of silicone resins in intumescent paints used mostly for protection of steel structures against fire will be presented based on literature review. Some examples of innovative applications for fire protection of other materials will be also presented. The effect of silicone resin structure and the type of filler used in these paints on the properties of the char formed during the thermal decomposition of the intumescent paint will be discussed in detail. The most frequently used additives are expanded graphite and organoclay. It has been demonstrated that silicate platelets are intercalated in the silicone matrix, significantly increasing its mechanical strength and resulting in high protection against fire.

intumescent paint | silicone resin | fire protection of steel structures

1. Introduction

Silicone resins and branched polysiloxanes with very good thermal resistance are widely used as components of coating materials to meet the requirements of different applications. These compounds can be used to coat various materials, including building materials, ceramics, and construction elements. One of the examples of demanding applications are steel and aluminum structures used in construction, which must be adequately protected against fire in order to maintain their load capacity for a specified period of time, enabling the evacuation and protection of the object. Under fire conditions, the temperature of steel structure elements rises very quickly, reaching the limit temperature in which a loss of mechanical properties occurs. The result is deformation of the structural elements and their collapse. Depending on the type of fire source and its intensity and the massiveness of the structural elements, the critical temperature of steel (450–550 °C) can be reached within a few minutes. The reason for the loss of mechanical properties of steel at elevated temperatures may be stresses related to thermal expansion [1]. Steel can also exhibit a steel creep effect when the structure is exposed to the simultaneous effects of elevated temperature and high stresses. Based on detailed studies, it was found that this effect occurs at temperatures above 400–500 °C, depending on the type of steel [2]. Comparing the thermal stability of both hot-rolled and cold-worked reinforcement bars, it was found that up to a temperature of 400°C, no significant changes in mechanical strength occur [3]. However, at higher temperatures, a clear reduction in the mechanical strength of cold-worked reinforcement bars was observed, being up to 10–15% at 600 °C. In addition, the residual mechanical deformation at 600 °C was 50% for hot-rolled specimens and about 150% for cold-worked bars, which is important for the strength of the structure during a fire. The role of passive protection of steel against fire is to create an insulating barrier that extends the time it takes to reach a critical temperature of steel to allow people to evacuate and firefighters to act. Depending on the type of structure, location of structural elements, and local standards, the required time of fire resistance of the structure is classified in the range from 15 min to 2 h.

Historically, the first way to create an insulating barrier against the inflow of heat was to enclose the steel structure in a concrete cover (thermal conductivity 1–3 kW/(m·K). The next applied solution was the use of spraying cement or gypsum masses filled with light porous material (which can expand under high temperature conditions), e.g., polystyrene granules, perlite, vermiculite, or mineral fiber materials. These solutions had very limited applications due to the weight of the insulating layer and corrosive properties of cement mixtures which require the initial protection of steel.

Good effects in protection of steel structures against fire are achieved through the use of intumescent paints capable of producing a sintered layer during a fire, isolating the steel structure from high temperature. The best protection of the structure can be obtained when the sintered layer is formed in a controlled manner with the formation of a layer with an appropriate thickness from 1 mm to 10 cm [4]. The basic ingredients of intumescent paint are carbonizable material, e.g., di-pentaerythritol, catalyst in the form of mineral acid or ammonium polyphosphate-APP, blowing agent (most often melamine), and a binder [5][6][7] on an organic or mineral basis. The most commonly used organic binders are chlorinated rubbers [8], phosphorus-containing styrene–acrylic copolymers [9], vinyl copolymers [10], epoxy resins (often in hybrid systems with phosphorus compounds) [11], and acrylic latexes [12][13] or epoxy resin-based binders [14]. The paint binder, in addition to its basic function, ensures good adhesion to the substrate throughout the entire process, as well as flexibility of the insulating coating. The binder is also a source of additional carbon in the insulating layer. Plasticizers and fibrous fillers enable the production of a sufficiently thick and mechanically stable foamed layer. All chemical reactions and physical changes during the swelling process must occur at the correct speed in the correct sequence.

Unfortunately, it should be noted that typical organic binders used to make intumescent paints have a number of disadvantages. First of all, organic binders undergo thermal decomposition with the release of toxic gaseous products. It also causes a deterioration of the thermal insulation properties of the coating because the sintered layer is cracked and has insufficient cohesion. An additional factor causing the imperfections of the sintered layer is a softening point that is too low and thermal decomposition of organic binders, which disturbs the formation of this layer [15]. All these factors can damage the coating during a fire and, consequently, give an insufficient protection of the structure [16][17]. Very good protection results for such structures can be obtained thanks to the use of silicone-based intumescent coatings. Silicones with a branched structure, including silicone resins or branched polysiloxanes, are characterized by very good thermal stability, which may facilitate adequate protection, because the loss of mechanical properties of steel usually occurs at a temperature of about 500 °C [18].

At this point, a second inorganic type of intumescent coatings based on alkali silicate [19] should also be mentioned. They are mainly used in the fire protection of wood. These paints swell on exposure to fire mainly due to endothermic loss of hydration water. Additionally, due to their ability to melt, they form a solid rigid foam consisting mainly of hydrated silica. Their use as protective coatings is limited and they are mainly used as firewalls. Therefore, they will not be discussed in this publication.

The aim of this review is to present the most important information concerning silicone fire-retardant intumescent paints based on a literature review made using the following keywords: intumescent paint, silicone resin, fire protection of steel or aluminum structures, silicone intumescent paint application. Literature review was made using the following databases: Web of Knowledge, Scopus, and Google Scholar. The research also covered Espacenet, Patentscope, and Google Patents, which resulted in the presentation of selected patents relevant to the subject. The overview is divided into the following main sections including discussion focused on the effect of silicone resin structure on its thermal stability, the effect of silicone resin structure, and the type of filler used in these paints on the properties of the char formed during the thermal decomposition of the intumescent paint and most important innovative applications of these paints.

2. The Effect of Silicone Resins Structure on Their Thermal Stability

The properties of silicone resins differ significantly from those of linear polysiloxanes. The main factors causing these differences are their branched structure and the presence of various types of organic substituents attached to silicon atoms by a Si−C bond. In the synthesis of polysiloxanes, monomers with different degrees of branching are used (see Table 1).

Table 1. Monomers with different degree of branching used in the synthesis of polysiloxanes.

Denotation	Stoichiometric Formula	Structural Formula	Degree of Branching
M	$R_3SiO_{1/2}$	R Me-Si-O- R	1
D	$R_2SiO_{2/2}$	R -O-Si-O- R	2
T	$RSiO_{3/2}$	R	3

		-O-Si-O- O	
Q	$SiO_{4/2}$	O -O-Si-O- O	4

where R: organic group.

The term ‘‘branched structure’’ means that the polysiloxane contains T or Q units in its chain. The measure of the degree of branching is the ratio of organic groups to silicon atoms (R/Si). The lower R/Si ratio is the higher content of the T units and the branched extent. In the thermogravimetric study of branched and linear polysiloxanes, it was found that thermal stability of branched polysiloxanes was higher as compared to linear ones [20]. The examined branched polysiloxanes were characterized by the degree of branching R/Si ranging from 1.2 to 1.5 and the molar ratio of the phenyl and methyl groups content expressed as moL/moL% ranging from 0/100 to 100/0. The branched polysiloxanes showed a solid residue upon decomposition at 800 °C, depending on the phenyl group content, amounting to 77.3–65.1 wt.% of the initial weight in nitrogen atmosphere and 66.5–40.5 wt.% in air atmosphere. The linear polysiloxane had a degree of branching of 2 and a 75/25 phenyl and methyl ratio, and the solid residue was 37.2 and 26.4 wt.%, respectively, under nitrogen or air. It was found in these studies that the value of the solid residue for a given group of polysiloxanes increased with the decreased content of phenyl groups. However, the solid residue value is not the only criterion for heat resistance. Temperature of degradation is also an important parameter. It is also known that methyl/phenyl branched polysiloxane showed the superior flame-retardant effect as compared to linear polydimethylsiloxane {PDMS) [21][22][23]. Higher thermal stability of methylphenyl polysiloxane as compared to PDMS was confirmed by the measurement of the onset temperature of degradation as nearly 400 °C for methylphenyl polysiloxane compared to 300 °C for PDMS. It is known that the presence of phenyl groups in the resin structure increases their thermostability to 200–250 °C for methylphenyl silicone resin (containing at least 20% of phenyl groups) compared to 180–200 °C for methyl silicone resins [24]. Methylphenyl silicone resins can be used as clear coats or with the addition of inorganic pigments as coating materials for long-term operation at 350 °C.

As shown above, the thermostability of methylphenyl silicone resins depends on their structure expressed by the degree of branching R/Si and on the content of phenyl groups. This gives a very good opportunity to select the resin with the most appropriate parameters necessary to create a good-quality sintered layer created by intumescent paint.

3. Innovative Applications of Silicone-Based Intumescent Paints

The significant progress in the technology of intumescent paints related to the introduction of new binders with increased thermal resistance, such as, for example, silicone resins capable of reacting with properly selected fillers, contributes to the constant trend of increasing the range of applications of these paints. This trend concerns not only the size of the market, but is also related to the development of new types of paints that give good effects not only on steel but also on other substrates requiring very good fire protection, such as plastics, fabrics, cellulose or wooden products. According to the report Research and Markets [25] the market for intumescent paints was valued at USD 927.6 million in 2018 and is anticipated to progress at a compound annual growth rate [CAGR] of 5.1% from 2019 to 2025. The greatest intensity of growth in the consumption of these paints is observed in the oil & gas sector and the automotive segment, especially in public transport and cargo vehicles. The continued development of the construction sector and large-scale infrastructure developments, especially in developing countries, also has a positive impact on the upward trend. Taking into account the types of paints and the applied binders, it was estimated that the water-based paints sector is developing the fastest, which is due to the increasing VOC limitations. The use of solvent-based paints in low-temperature and high-humidity areas to achieve a decorative finish on complex shapes and to improve adhesion and high water resistance will also increase due to the good properties of these paints. Taking into account the type of binder, the highest growth dynamics is observed in epoxy-based paints. This also presents an opportunity for the increasing the use of silicone resin emulsion binders, which have been shown in several of the publications discussed above to significantly improve the properties of such paints containing hybrid epoxy-silicone-based binders.

In a Goldstein Research [26] report published in May 2020 the trends of the intumescent paints market were similarly assessed. According to this report, the oil and gas industry is the dominant segment of intumescent paints end users, accounting for over 50% of the global market share in 2017. In addition, it is expected to grow by 5% from 2017 to 2030. The fastest growing industry of intumescent paints users is construction with a CAGR of 5.1% for the period from 2017 to 2030, which is caused by large infrastructure projects in China and India. Another area with significant consumption of these paints is the automotive segment, due to the need for a thermal barrier and high temperature protection for the engine in vehicles to ensure increased safety.

It should be noted that the intumescent fireproof coating is one of the easiest and most effective methods of protecting materials, used not only for metal surfaces, but also for plastics, steel, wood, electric cables and polymer composites. This method of protection does not cause chemical modification of the substrate, but rather the formation of a protective layer that changes the heat flux acting on the substrate and may inhibit the temperature of its degradation, ignition or combustion [27]. Even inherently non-combustible steel, when exposed to high temperatures, exhibits a significant reduction in strength and stiffness, which, according to observations made during the collapse of several structures during fires, has a detrimental effect on the stability of the structure [28]. There are a number of types of intumescent coatings on the market. The limitations and recommendations associated with their use should be always considered [29][30]. This should be taken into account in special cases concerning especially paints based on organic polymers. Modification of organic binders with silicone resins improves flame resistance. A number of such solutions are described in patents. So far, some silicone-based intumescent paints [31][32][33] have been patented to significantly extend the fire resistance of the protected substrate. The Korean patent [31] describes the use of a silicone emulsion as an acrylic binder modifier, which improved the properties of intumescent paint. A steel surface protected with the described composition can be kept at the temperature below 649 °C for 2 h. A three-hour resistance time is demonstrated by the silicone resin binder composition described in patent [32], which can be used on rebars, crossbeams, pillars, and ferroconcrete structures in a building. The created intumescent layer shows the maintenance of insulation performances thanks to strong adhesion and wear resistance. Very good results are also reported in patent [33] for intumescent paint with silicone resin binder. Tunnel fire-proof intumescent paint based on an acrylic-silicone binder with very good fire-retardant properties was obtained thanks to the addition of silica nanoparticles [34]. This paint is characterized by the appropriate thickness of the coating layer, adhesion and fire resistance. The intumescent paint based on a silicone acrylic emulsion and the spirocyclic phosphate can be applied to all cellulose textiles [35]. The obtained protective layer is characterized by high mechanical strength, good waterproof and weather resistance and smooth coating surface.

The stability of the carbonized protective layer is crucial to ensuring fire safety in high-rise buildings. It was found that the addition of non-purified fullerene-containing soot with different structure (C60, C70 etc.) and graphite's microparticles allows to obtain a protective layer with increased strength [36]. The used fillers can have a great influence on the properties of intumescent coatings [37], because the carbonized layer is basically a carbon matrix that can readily accept other carbon materials such as graphite and fullerenes that have proven themselves as reinforcement additives [38], which can protect the charred layer from damage [39].

Intumescent paints are also used to protect plastic surfaces. Beaugendre et al. [40] investigated the properties of protective coatings obtained from a paint containing a mixture of epoxy/silicone resins, a curing agent and either iron oxide or calcium carbonate as fire retardant filler. The obtained results confirmed that the use of these coatings for the protection of polycarbonate allows the creation of a protective barrier limiting the spread of flame, which reduces the flammability of elements made of polycarbonate and reduces dripping of burning material during a fire. It was found that the obtained good properties of the protective layer are related to the incorporation of chalk and iron oxide into the structure of the coating formed during the combustion of epoxy silicone binder. A special intumescent paint creating a flexible and transparent coating on the coated surface is described in the US patent [41]. This composition contains organic resin and/or silicate binders and is designed for the protection of flexible laminates requiring transparent top layers such as electro-optical displays or photovoltaic tiles. Kandola et al. [14] investigated the thermal barrier and fire reaction properties of three commercial intumescent coatings derived from paints containing epoxy binders on glass fiber-reinforced epoxy composites. On the basis of measurements with a cone calorimeter, their thermophysical properties in terms of heating rate and/or coefficient of expansion depending on temperature were determined and correlated with thermal conductivity. The innovative applications of the silicone-based intumescent paints on different substrates showing drawbacks and advantages are summarized in Table 4.

Table 4. The innovative applications of the silicone-based intumescent paints.

Type of Silicone Intumescent Paint	Protected Substrate	Drawbacks or Advantages	Ref
Acrylic binder modified with silicone resin emulsion	Steel	Improved thermal stability. Protected steel surface withstands temperature up to 649 °C for 2 h	[31]
Styrene-modified acrylic copolymer resin containing a silicone-modified acrylic resin that improves fire resistance	Structural elements and reinforced concrete structures	Very good fire resistance (up to 3 h) due to strong adhesin and wear resistance of intumescent layer	[32]
Silicone resin binder obtained by reacting epichlorohydrin with polysilanol compound. Glass flakes added as a filler	Steel and reinforced concrete structures	Can be applied as an alternative material instead of plaster, vermiculite spraying, and concrete fireproof walls	[33]
Acrylic-silicone binder	Tunnel fire-proof protection	The bonding strength is 0.5 MPa, and the fire resistance limit is 90 min.	[34]
Silicone acrylic emulsion containing spirocyclic phosphate intumescent flame retardant	Cellulosic textile	Long burning resistance time, high mechanical strength, good waterproof and weather resistance and smooth coating surface. A preparation technology is simple in process and convenient in operation	[35]
Silicone resin binder, non-purified fullerene soot, graphite	High-rise buildings	Reinforced structure of intumescent layer	[39] [38]

microparticles			[37] [36]
Epoxy-silicone binder, $CaCO_3$ or Fe_2O_3	Polycarbonate	Formation of intumescent layer limiting the spread of flame. Reduced dripping of burning material during a fir	[40]
Epoxy-silicone resin binder, $CaCO_3$, Fe_2O_3	Electro-optical displays or photovoltaic tiles	Formation of flexible and transparent coating	[41] [31]
Aqueous organic polymer dispersion and silicone resin emulsion	Steel, aluminium, wood, concrete, electric cables and pipes, or for coating open steel profiles, closed and/or castellated profiles, or for workshop applications.	Easy to application intumescent paint forming protective layer characterised by very good mechanical and thermal properties	[42]
Multilayer epoxy resin based intumescent paint. Silicone resin as binder for the top layer	Different surfaces metal, wood, plastics used in construction	The disadvantage is the necessity to apply the paint twice. The first layer is based on epoxy resin and the second layer is based on silicone resin	[43]
One or more crosslinkable silicone polymer	Applicable to products formed for fire wall linings, fire partitions, screens, ceilings or linings, structural fire protection, fire door inserts, window or door seals, intumescent seals, in electrical switchboard cabinets or cables. In one cable application, the composition may be used as the extruded intermediate material	Very good mechanical properties and high temperature stability	[44]

Intumescent composition comprising a polydimethylsiloxane (A) of degree of polymerisation at least 300 siloxane units and expandable graphite and a titanate catalyst	Protection of a metal, wood or plastics substrate exposed to fire risk from hydrocarbons	Reinforced structure of intumescent paint. Very good thermal insulation and adhesion to different substrates	[45]

Good durability of the coatings and adhesion between all types of coatings and the substrate were found, indicating the possibility of using intumescent paints to protect glass fiber-reinforced epoxy composites. It can be stated that the protective layers formed from coatings obtained from intumescent paints are increasingly used not only to protect steel structures but also other materials such as building materials and plastics. There are a number of original recipes of these compositions enabling the protection of buildings, e.g., tunnels, vehicle protection and even flexible laminates used in displays in modern electronics.

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