Fire-Protective and Flame-Retardant Coatings – A State-of-the-Art Review

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ABSTRACT: This review covers mainly intumescent coatings, with briefer discussions of non-intumescent organic fire-resistant coatings and cementitious inorganic coatings. Emphasis is placed on the more recent developments, and the more recent patent literature is surveyed. Modeling and optimizing are covered both from basic and applied aspects. The chemistry of the production of a foamed char barrier is discussed. Enhancing the performance by adjuvants and choice of binders is shown to be possible. The important interactions of ammonium polyphosphate with other components such as titanium dioxide are described. Testing is briefly discussed, as are some shortcomings of present-day coatings, such as limited water resistance, and some opportunities for improvement.

KEY WORDS: intumescent coatings, spumific, carbonific, ammonium polyphosphate, heat transfer, melamine, char, adjuvants, silicates, borates, titanium dioxide, expandable graphite, binders, ceramic coatings, textile coatings, firestops, gelcoats.

INTRODUCTION AND SCOPE

PASSIVE FIRE PROTECTION includes coatings and firestops, as well as the use of inherently flame-retardant materials. Flame-retardant plastics and textiles have been covered in a recent book by Weil and Levchik [1]. Fire-retardant coatings for wood have been briefly reviewed in the

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broader context of fire safety of wood construction by USDA Forest Products Laboratory researchers in the 2010 Wood Handbook [2]. Wood coatings more often are designed to retard ignition and rate of burn rather than to provide the fire-resistive barrier which is more typical of steel coatings.

Traditional fireproofing coatings are cementitious coatings, based on Portland cement, magnesium oxychloride cement, vermiculite, gypsum, and other minerals. Fibrous fillers, supplementary binders, and density-controlling and rheology-controlling additives are typically mixed with water on site and applied by spraying during steel construction at thicknesses of one-half inch or more. The Underwriters Laboratories Fire Resistance Directory calls them Spray Fire Resistant Materials (SFRMs). Some of these coatings can be applied onto a flammable substrate by the use of rollers and/or a moving belt. These coatings can provide fire protection from one-half to several hours by water release and thermal insulation effects. They are low in cost and easy to apply, and some are resistant to weather exposure. However, because of their weight, thickness and poor esthetics, they limit architectural design. Building designers avoid them for visually exposed steel. They may also be dislodged in a violent fire. Further discussion of these mineral coatings is outside the scope of the review, as are rigid mineral-based boards, fire blankets, or loose-fill flame-retardant insulation as passive fire protection. A useful although brief discussion of SFRMs as well as intumescent coatings and their UL classification is found in a Carboline paper [3]. Firestops and flame-retardant gelcoats are briefly discussed in this review.

This review will put the main emphasis on coatings, particularly intumescent coatings (which swell to a thick insulative foam when heated above a critical temperature), but will briefly discuss other types of coatings which are flame retardant but not intumescent. Both these types of non-mineral coatings can be applied by qualified painters, and can offer good appearance and durable surfaces. The US market has been underdeveloped for intumescent coatings for steel in buildings because of the predominance of concrete construction, relative cost, and possibly lesser familiarity by architects.

Another main classification of fire-protective coatings is based on their desired performance, namely: (1) those that increase the fire resistance as defined by ASTM E1119 for buildings or by ASTM E1529 for hydrocarbon fires and measured in terms of time, i.e., 1 h, 2 h, etc., and (2) those that reduce the flame spread of the combustible substrate, such as wood, as measured by the flame spread index of ASTM E84 in the USA. Fire-protective coatings can also be classified from the standpoint of the type of fire being protected against: (1) the ‘wood fire’ such as
might occur from burning furniture, paper, cloth, etc., (typically represented by the E119 test, discussed later), and (2) the ‘hydrocarbon fire’ from burning petroleum (typically assessed by the E1529 test, also discussed later). Both classifications have considerable overlap.

Typically, coatings protective (or retardant) against cellulosic-type fires are applied in thin film coats up to 1.5 mm (60 mils) thick. These coatings are usually not very weatherable; so, for outdoor applications, a protective topcoat is needed. Coatings protecting against hydrocarbon fires are typically two-component (usually epoxy) systems applied solvent-free at 8–10 mm (320–400 mils) per coat often through separate heated lines with an in-line static mixer at the spray tip. The steel surface should be prepared by an abrasive blast, and then an anticorrosive primer should be applied. After application of the fire-protective coating, a topcoat (for example, an acrylic polysiloxane finish) may be applied. These coatings may be applied off-site or after the steel framework has been erected. A properly applied coating of this type is suitable for offshore oil and gas facilities, being quite resistant to hydrocarbons and to seawater.

BACKGROUND

The classical review of intumescent coatings is a 1971 paper by Vandersall [4] (Monsanto). He presents the early history and the detailed course of development of commercial intumescent coatings, mostly based on a char-forming carbonaceous material (‘carbonific’), a mineral acid catalyst, a blowing agent (‘spumific’), and a binder resin. This review is replete with formulations and is still a rich source for ideas for formulation improvement. At the time of Vandersall’s review, typical commercial intumescent paint formulations contained several pounds per gallon of intumescing components, and required thick and costly coatings. Much empirical research has been done in industry and a few academic laboratories to optimize intumescent coatings, to find alternative char-formers, catalysts and blowing agents, optimized binders, activators, and residual barrier-forming additives. Parallel work has been done outside of the coatings area to apply the intumescent approach to flame-retarding polyolefins, olefin copolymers, elastomers, and ‘firestops’ (barrier materials for closing wall apertures). We have reviewed polyolefin flame retardancy previously in this journal [5] and, with elastomers included, in a subsequent book [1]. In view of this prior coverage, this review will concentrate on coatings with some attention to firestops.
More recent reviews have covered, usually not in the detail of Vandersall, the commercial applications of fire-retardant and fire-resistive coating. It is our intention to emphasize the more recent developments and those which seem to be of greatest practical value. The theoretical and basic topics are covered by reference to published studies without repeating them in any detail.

A useful review from a commercial viewpoint has been presented by a marketing manager in this field [6]. The importance of architectural design – the esthetics of exposed steel – is discussed, as well as the question of on-site versus factory application.

Fire protection engineering overviews, comparing cementitious fire-protective coatings to intumescent coatings, are available from both before [7] and after the 9-11-01 disaster. Subsequent to 9-11-01, much attention was given to this question; a critical review by the National Institute of Standards and Technology was published in 2004 [8] and is available as a book.

A 2007 review [9] of specialty coatings for fire protection covers the entire range of fire-retardant and fire-protective coatings, with realistic discussion of needs, markets, market dynamics and trends, codes and other regulatory issues, and types of products available, with profiles of major US suppliers and their product lines.

**NON-INTUMESCENT FIRE-RETARDANT COATINGS**

A broad but not highly detailed overview of flame-retardant/fire-resistive coatings is presented by Green [10] who showed that even conventional paints can reduce flame spread below that of an unpainted flammable substrate, but for demanding situations such as on shipboard, coatings deliberately formulated for low flame spread index are preferred. On shipboard, paint is repeatedly applied to prevent corrosion, and fire-resistant coatings using halogen–antimony flame-retardant systems are commonly used. The halogen component may be a vinyl chloride–vinyl acetate copolymer, a chloroparaffin, or a chlorine-containing alkyd. Formulations are given for fire-retardant latex paint and alkyd-based paint. Formulations of this sort used by the US Navy and improvements in the 1990 period have been described in 1996 [11].

A typical shipboard paint of a type probably still used by the Navy (MIL-DTL-24607B) [12] contains a chlorinated alkyd such as Reichhold’s Becksol® 91160-00, titanium dioxide, alumina trihydrate (ATH), magnesium silicate, calcium borosilicate (Halox® CW-2230), calcium metaborate (Buckman’s Flame Block® BL-381, various pigments,
thixatropes, surfactants, solvents (such as Oxychem’s Oxsol® 100, \( p \)-chlorobenzotrifluoride), and driers shown in the specifications.

Coatings using high mineral loadings are another means for attaining flame resistance. A formulation of 18.6% rutile (\( \text{TiO}_2 \)), 12.7% barium metaborate, 8% aluminum silicate pigment, 21.1% polyvinyl alcohol (PVA), and several wetting agents and dispersants with 25.2% water was published for an interior flat wall paint in 1992 [13].

Resistance to ignition and flame spread on wood is said to be provided by an aqueous coating using ATH, antimony trioxide, and calcium carbonate with a vinylidene chloride–acrylate binder in a 1987 patent [14]. The coating is said to be suitable for exterior application.

A German research institute [15] has developed a fire-protective coating for wood based on ceramicizing compositions of sodium borate and silica plus optional phosphorus ester or salt components, using various aminoplast or urethane resins as binders.

A commercial additive CEEPREE®, a borosilicate glass with low softening point, has been available since its original development at ICI [16]. This additive is useful, for example, in mastics for protection of steel against very hot (fuel) fires, providing some protection after organic material has burned away [17].

Protection of metals from corrosion while avoiding fire propagation can be accomplished by a thin coating of ethylene–chlorotrifluoroethylene copolymer (Solvay Solexis’s Halar®), which chars when exposed to fire. Even coatings as thin as 10 mils can be effective [18].

**Basic Studies on Intumescent Coatings**

Basic research has been of two main types, one emphasizing the heat transfer aspects and the other the chemical aspects. A broad review dealing with both aspects, as well as practical considerations, has been published by a University of Lille group [19].

**Heat Transfer Studies With Intumescent Coatings**

A group experienced with aerospace vehicle protection developed a semi-empirical computer model of the intumescent coating performance taking into account mass and heat transfer, swelling kinetics, and the reradiation of incident energy when a highly emissive char was formed. Experimental weight loss measurements and estimated thermophysical and chemical parameters were used as input, and the model was shown to predict backface thermal histories to within 20% of the experimentally measured values. Total expansion and rate...
of expansion were found to be important parameters for providing thermal protection [20].

Another group with aerospace background conducted an extensive experimental program together with a simplified heat- and mass-transfer modeling (a ‘frontal model,’ assuming a thin pyrolysis region which moves from the coating’s surface to the substrate) [21]. The experimental work used a heat source typical of aviation fuel fires and measured the temperature–time history of the substrate. A range of coatings were studied; classical intumescents as well as silicate–borate systems. One salient conclusion was that the binder is critical. Another was that large expansions are not necessary and can even be detrimental if the char becomes too frangible. The utility of the frontal model was confirmed.

A related study confirmed the utility of the thin zone model, and mathematical transforms reduced the model to one which was easily amenable to numerical analysis. It was shown that although endothermicity of the foaming process is helpful, it is not essential and the model fits well to experiment if adiabatic ‘tumescence’ is assumed [22]. A later modeling study [23] assumed the intumescent reaction to be analogous to a phase change process occurring over a finite temperature range and experiment showed that the substrate temperature could be accurately predicted by suitable choice of latent heat and temperature range for the intumescent reaction. The model of reference [22] can be taken as a special case of the later [23] model.

A subsequent Russian study [24] takes more account of the local viscoelastic properties of the foaming mass, heat conductivity, and the chemical kinetics. Using a new mathematical algorithm developed by these workers, a better fit was obtained of the computed data to the experimental data on a boron-containing intumescent phenol–formaldehyde coating. New observations on the morphology of the foam also provided insights into the details of the intumescent process.

Basic studies in Russia have also been done on particular features of intumescence. The effects of viscosity and surface tension, and of the dispersity of solid particles have been examined [25], and the combustion characteristics of the char were also studied [26].

The effect of a surface coating of polytetrafluoroethylene on an otherwise intumescent coating was shown, interestingly, to prevent or retard the intumescence but nevertheless a heat-protective char coating was formed [27].

A detailed comparison and modeling by Koo [28] of the fire-protective properties of two commercial intumescent coatings led to the conclusion that the better performing material had larger expansion and no contraction as well as lower thermal conductivity.
A two-dimensional model was developed in an Australian engineering school [29] for studying the heat transfer through epoxy subliming and intumescing coatings. Two different commercial coatings were evaluated in regard to temperature and surface profiles under flaming conditions and found to fit well to the model provided that delamination did not occur. A later model by the same researchers [30] incorporated kinetic equations and produced a good fit of conversion under isothermal conditions, except during initial stages of intumescence and sublimation. Further refinement of the model [31] showed that atmospheric oxygen content is a major factor.

A generalized pyrolysis model was developed more recently at Berkeley [32] which can cover a charring (wood) substrate, a non-charring poly(methyl methacrylate) substrate, and intumescent coatings, and has an encouraging correlation to experimental data.

A model for the intumescence process with ammonium polyphosphate (APP) and pentaerythritol in polypropylene (not specifically a coating) was developed by Lille researchers [33] taking into account kinetics and phase changes. Reasonable correspondence of computer and experimental temperature profiles lend support to the model. Intumescence was shown to occur mainly between 280°C and 350°C, and then degradation of the intumesced coating between 350°C and 430°C by the further action of the flame. Above 430°C, structural changes occurred in the char. Further modeling by this group [34] took account of anisotropy from the presence of carbon nanotubes, non-woven fabrics, and intumescent paint on steel, using the modeling and simulation heat transfer module of a particular software package. A further study by this group [35] was directed toward a broader elucidation of the mechanism of action of intumescent coatings.

A mathematical model designed to be applicable to systems for protecting against fast violent heating and explosions as encountered in military situations was developed in France [36]. It showed promise but was said to need further studies to improve accuracy.

A study published in 2009 discussed the effects of partial fire protection on temperature development in steel joints protected by intumescent coating [37].

**Heat Transfer and Combustion Kinetics of a Non-phosphorus Intumescent System**

An intumescent fire-resistance coating for steel based on polychloroprene, ATH, and expandable graphite was studied and shown to
undergo three consecutive first-order steps on heating to 873 K – release of water from ATH, release of hydrogen chloride, and release of gases from the graphite expansion [38]. All these processes retarded the heating of the steel substrate.

**Optimization Studies of the Ingredient Ratio of APP Systems**

In a Russian study, the optimum weight ratio of APP (or some melamine organophosphonate salts) and polyol for both thermal protection and oxygen index was found to be 7:3 for pentaerythritol, glycerol, and PVA [39].

An intricate optimization study involving computation as well as experiment was published by Horacek [40] in 2009 in which he postulated, and in some cases supported experimentally, a number of plausible stoichiometric relationships of APP, polyol, and melamine, and titanium dioxide as well as heat of combustion relationships. The methodology is intricate and cannot be easily summarized but the conclusion was that a lower temperature-reacting polyol would be advantageous; glycerol used along with the pentaerythritol was said to improve the performance, allowing lower temperature (300°C) for maximum expansion whereas with the pentaerythritols, maximum expansion required 390°C. The implication was that the required dry film thickness and number of coats could be reduced.

**Mechanical Strength of Intumescent Chars**

The mechanical stability (measured work required to crush the char from a urea–formaldehyde intumescent formulation) was also found at the optimum APP-to-polyol ratio, but (not surprisingly) a more expanded foamed char was easier to crush. The mechanical strength of various types of chars in the hot and cold states was investigated by a Russian group [41,42]. The technique used a controllable crushing device developed for food (presumably baked goods) testing. In a further study by this group, mathematical modeling was done on the char formation; smaller pores were found to be beneficial to mechanical stability [43]. A mathematical model of the bubble phenomena was developed by these researchers [44]. Radiant heat within the bubbles was shown to be the main mode of heat transfer [45]. An apparently more predictive algorithm for modeling the intumescence process was developed by a Russian–Kazakh group taking account of the local change of viscosity (found from viscosity isotherms) which affects local expansion [24].
A systematic study at the University of Lille (2006) [46] used thermogravimetric analysis (TGA), rheometry, and mechanical strength testing, with statistical methodology, to address the problem of balancing the desirable expansion with the desirable strength of the intumesced foam. The results correlated well with industrial furnace tests. A more recent study by the same group [47] of the kinetics of pyrolysis led to development of a predictive model for the degradation at different heating rates.

**ADJUVANTS IN INTUMESCENT SYSTEMS – ACADEMIC AND OTHER BASIC STUDIES**

Much development of such systems has been outside of the coatings field and rather, directed to thermoprocessed polymer systems such as wire and cable jackets, building materials, and automotive or aerospace plastics. Nevertheless, it is quite likely that non-coating findings may be applicable to coatings and, at the risk of some overlap with our previous review [5] and book chapter [1] on polyolefins, this review will encompass them.

Researchers at Lille (France) found that zeolites such as 4A (Na A zeolite) has a very strong synergistic effect in a classical APP/pentaerythritol intumescent system in polyethylene. The zeolite encourages formation and stabilization of ‘phosphocarbonaceous’ structures giving an improved intumescent shield, which also decreases the fuel feeding the flame [48]. The same researchers found a very helpful effect of including polyamide-6 in an intumescent APP/ethylene–vinyl acetate system, where the polyamide-6 and APP interacted to form a second heat-protective shield in addition to that formed from the ethylene–vinyl acetate APP interaction [49].

Although not explicitly on coatings, a relevant study was done in polypropylene by University of Turin researchers in collaboration with Himont researchers [50] on the effect of a series of inorganic fillers in an APP–aminoplast resin intumescent system. Calcium phosphate, being unreactive, was found not to spoil the flame-retardant action, whereas talc and calcium carbonate, which modified the chemistry of the system, were deleterious. A layer of polyphosphoric acid on the char surface was beneficial to its insulating action. The heat reflectance characteristics of the char were also shown to be of importance.

A subsequent study at Hoechst Celanese [51] also done in molded polypropylene, compared and interpreted the effects of several inorganic additives on char formation in an intumescent system based on APP
and a char-forming polyol. Targeted features for an optimum char were
dense compact outer crust with no porosity, interior sections with a
highly ordered cellular network, and mass. Tin dioxide was antagonistic
by chemical interaction without bridging of polyphosphate, causing
porous flaky char, whereas TiO$_2$ was beneficial, attributed to bridging of
the polyphosphate.

A research group at a Polish institute [52] recently claimed a
beneficial performance effect in APP-based intumescent coatings by
addition of 0.2–5% nano-scale silica and also by addition of a
hydrophilicizing surfactant 2,4,7,9-tetramethyl-5-decin-4,7-diol (Air
Products Surlyn® 104).

Chemistry of the Classical Char-Former, Char-Catalyst,
and Blowing Agent Systems

The general outlines of this intumescent coating chemistry were
described in the classical Vandersall review. In its most general and
oversimplified summary, an acid-generating catalyst, most commonly
APP reacts with a polyol to initiate dehydration to a carbonaceous char,
and a blowing agent such as melamine or an HCl-releasing polymer or
additive generates gas in the molten mass to make a foam which
solidifies from the melt to make a heat- and vapor-transfer barrier.

Subsequently, detailed studies of the chemical steps were made by
Camino’s group in Turin (1984–1990) [53] and by the research group at
University of Lille (2004) [54]. Both groups relied heavily on thermal
analysis and spectroscopic methods. In this review, we will not repeat a
discussion of this readily accessible work, but to address some of the less
obvious features.

The Behavior of APP When Heated

Based on laboratory-scale thermal studies, such as by the Turin
researchers [55], APP loses ammonia along with water, and in several
stages forms a crosslinked polyphosphoric acid. Actually, the thermal
behavior of APP is quite complex and much depends on whether the
ammonia is in any way constrained. With even light constraint, as in a
loosely capped vessel or a polymer matrix, enough ammonia remains
chemically bonded such that in the extreme case, the end product is a
ceramic-like material, phosphorus oxynitride (PON)$_x$ [56–58]. The
intermediate steps seem not to have been well investigated although
the formation of a P–N bonded glass has been noted when an APP is
held in a melt with a constraint on ammonia loss.
Thermal analysis studies by the Turin group [55] and by Taylor and Sale at Manchester (1992–1993) [59,60] indicate that with release of ammonia and water from APP, the reaction is complex and involves competing crosslinking reactions possibly forming P–N–P bonds (P–O–P bonds should also be considered). In the typical intumescent formulation, APP can react with a phosphorylatable substrate such as pentaerythritol and with a reactive amine such as melamine. Melamine can not only be phosphorylated on the NH$_2$ group but can also form a melaminium salt structure with any phosphorus acid group or even merely by displacing ammonia from the ammonium structure. Thermal analysis shows that melamine phosphates or polyphosphates are relatively more stable thermally than APP.

**Variations on APP**

APP is a complicated material, covering a wide range of molecular weight and having insoluble higher molecular weight versions besides the water-soluble, low molecular weight form. A review is available from a leading European manufacturer [61]; in it, X-ray diffraction diagrams are given for five crystal forms, as well as solubility data on the main commercial high-molecular weight form II and various coated varieties of form II. A more recent Japanese study [62] also provides X-ray diffraction data on the five forms, and indicates methods of preparation; moreover, the Japanese researchers show that one of the less common forms (V) may be a better flame retardant than the others, a surprising result calling for more research.

Commercial forms of APP are several. A water-soluble, low molecular weight version is used mainly for non-durable cellulosic flame-retardant textile finishes. A water-insoluble but relatively hydrolysable version, Phase I, is sometimes used in coatings and particularly in applications where water resistance is not needed. A higher molecular weight more water-resistant Phase II APP is preferred for use in coatings. Several coated Phase II APP are available from Clariant, Budenheim, and Asian producers, with both hydrophilic and hydrophobic coatings. A surface-reacted APP where melamine has been used to replace some of the ammonium cations represents another water-resistant grade, and may be further coated with an amino resin to give a still more water-resistant APP, at a higher price.

A Hoechst patent [63] claims that APP of degree of polymerization of 600–800 and NH$_4$ :P mole ratio of about 1 is best in water-based coating formulations from the standpoint of low solubility in water and good dispersability with minimal settling.
A Clariant patent [64] claims combinations of APP with melamine polyphosphate which have improved stability under high humidity (tropical) conditions, suffering less loss of ammonia. This patent discloses many diverse formulations with a variety of binders. A similar object is achieved by including other melamine salts or guanidine salts as shown in a related Clariant patent [65]. A combination of APP and dicyandiamide phosphate is proposed in a more recent patent [66] as the active ingredient in a water-based epoxy intumescent coating for wood.

The Thermal Behavior of Melamine Itself

A typical component of intumescent coatings is melamine, which is often said to be the blowing agent (the ‘spumific’). Actually, the role of melamine is complicated, and even the thermal behavior of the material by itself is complicated, as discussed in our 1995 review [67]. When heated in a small amount where vapors can escape without constraint, melamine totally sublimes in the 250–350°C range, as shown by the TGA curve published by Taylor and Sale [59,60]. However, if the vapors are in any way constrained as, for instance, by heating of melamine from the bottom in a deep layer, part of the melamine sublimes and part loses ammonia and goes through a series of ammonia-losing condensations to yield –NH– linked two, three, and multiple ring condensation products, called melam, melem, and melon, respectively. The sublimed melamine vapors and the released ammonia are poor fuels and probably flame inhibitors, even though ammonia gas is per se flammable. Melamine vapor is said to be capable of endothermic dissociation to cyanogens [68], also a poor fuel; whether that chemistry and heat-sink effect play a role in the flame-retardant contribution of melamine has not been established.

It has been found that in intumescent coatings containing melamine, further addition of a chloroparaffin aids the performance. Lille researchers [69] found that melamine or its thermal condensation products (discussed in some detail) caused the dehydrochlorination of the chloroparaffin and that this was a step in the effective action. It was further suggested that PVA or polyvinyl acetate could be substituted for the chloroparaffin.

Interaction of Melamine With Phosphorus Ingredients in Intumescent Coatings

Obviously, melamine being a base albeit a rather weak one, can react with phosphorus acid species made available, for example, by
decomposition of ammonium phosphate, or it may even displace some ammonia from the ammonium salt to directly make melamine phosphate salts.

Melamine phosphate, pyrophosphate and (later), polyphosphate are all commercially available and they find use in intumescent coatings. A very thorough 1979 review by Kay et al. [70] covers both the combinations of melamine with phosphate retardants, their interaction, and the use of pre-made melamine phosphates. Our later review (1994) [71] covered the coating applications. Advantages are shown for melamine pyrophosphate over melamine phosphate in both thermal barrier formation and lower water solubility. Formulations using various binders are discussed, and details of representative water-based formulations are given using vinyl acrylic emulsion and polyvinyl acetate emulsions with performance information. Formulations using melamine phosphates and APP together are discussed.

Melamine orthophosphate dehydrates to melamine pyrophosphate and thence at 290°C and above to melamine polyphosphate. Melamine polyphosphate can serve as both blowing agent and as a substance (or its thermolysis products) contributing to the foam layer as a coating intumesces [72]. Further heating under laboratory conditions at above 600°C can eventually lead to (PNO)ₓ, a crosslinked solid, although it has not been established that this higher temperature chemistry plays a significant role in intumescent coatings under fire conditions. (PNO)ₓ is probably too stable and infusible for use as the only phosphorus component in a typical intumescent coating although we found that it may be effective in systems where it can interact with a polymer such as a polyamide [73].

Variations of Melamine Phosphate

A hybrid salt composition made by the reaction of phosphoric acid with melamine and monoammonium phosphate is said in a 1993 patent [74] to substantially reduce the solubility of ammonium phosphate while retaining its low thermal dissolution (activation) temperature. A number of water-based intumescent paint formulations are shown.

Other Phosphorus Compounds in Intumescent Coatings

Chloroalkyl phosphates and phosphonates have been reported as useful in intumescent coatings, even coatings which also contain inorganic phosphates such as APP; the organic phosphate or phosphonate esters can provide plasticity, better coating properties, and
can serve as blowing agents and (by breaking down to phosphorus acids) charring catalysts. Some formulations disclosed in patents show use of monophosphates such as tris(2-chloroethyl) phosphate [63]. However, chloroalkyl phosphate and phosphonate oligomers with more than one phosphorus ester group per molecule such as Phosgard® C22R or 2XC20 (former Monsanto, now Albemarle) and Fyrol® 99 (former Stauffer, Akzo Nobel and Supresta, now ICL-IP) have generally been preferred. An early example shows the use of Phosgard® C22R or 2XC20 in an epoxy-based intumescent coating which also contained APP and melamine phosphate or guanylurea phosphate [75]. This patent, which shows complex formulations, also claims a performance advantage of having the decomposition temperatures of two of the active ingredients (either the P or the N component) at least 50°C apart. Substantially, halogen-free systems may use triaryl phosphates such as isopropylphenyl diphenyl phosphate (ICL-IP’s Phosflex® 31L or a similar Chemtura Reofos®) to provide plasticity.

Partial esters of polyols, notably of pentaerythritol and glycerol, are made by reaction with polyphosphoric acid and subsequently cured with epoxy resins and melamine formaldehyde resins to make clear intumescent varnishes on metal, wood, and textiles in a 1995 patent [76]. Further optimization of the coating properties, such as improved flexibility, is said to be achieved if a partial phosphate polyol ester made from tetrahydrofuran or 1,4-butanediol is part of the polyol phosphate reactant [77]. This patent application has a lengthy discussion of the history and rationale behind this versatile family of phosphorus-based intumescent coatings.

Two-component intumescent coatings of the mixed glycerol/pentaerythritol acid phosphate type, cured with aminoplast resins, are said to be especially suited for flame-retardant coating of fiberglass mats [78].

A patent application of Leigh’s Paints [79] discloses the use of diglycidyl methylphosphonate, triglycidyl phosphate, bis[2-(methacryloyloxy)ethyl] phosphate or dihydroxaphosphaphenanthrene oxide (DOPO), or preferably an adduct of DOPO with an epoxynovolac, in intumescent coatings especially for steel.

**Char-Producing Ingredients**

Many of the older formulations use pentaerythritol as the char former ‘carbonific’ in conjunction with APP as the charring catalyst. However, it is somewhat water soluble and the less-soluble although more expensive dipentaerythritol is often preferred. In a published comparison of pentaerythritol to di- and tripentaerythritol using rheological
measurements [80], it was found that pentaerythritol was the most
effective in intumescing sooner and keeping the substrate temperature
down longer. On the other hand, the temperature at which embrittle-
ment started was higher for the di- and tri-pentaerythritol; so, this
feature could be of value in lessening the lack of high wind resistance
and the high-temperature cracking – faults of intumescent coatings,
especially on cylindrical steel columns.

Lower cost cyclic formals (1,3-dioxanes) which are byproducts of
pentaerythritol manufacture have been shown by Perstorp [81] to be
useful as replacements for the pentaerythritols in intumescent coatings.

Another excellent char former is \textit{tris}(hydroxyethyl) isocyanurate
(THEIC), but this is also water soluble; therefore, polyesters derived
from THEIC are shown as preferred by Hoechst in epoxy-based
coatings [82].

Other ‘carbonific’ (char-forming) additives have been synthesized.
A Chinese university group [83] describes preparation and testing of
an ethanolamine–aminotriazine oligomer in a polyurethane intumescent
coating. The formulation had good rheology and the resultant film had
good thermal stability.

A Polish study [84] was done to arrive at effective intumescent
coatings for wood. In this study, dextrin (a starch product) was part of
the char-forming system, supplementing a urea–dicyandiamide–formal-
dehyde resin catalyzed by APP. Starches, sugars, and cellulose powders
are often mentioned in lists of char-forming ingredients for intumescent
formulations.

**The Role of Titanium Dioxide in Intumescent Coatings**

\textit{TiO}_2 is shown in many intumescent formulations. Besides its use as
a white pigment, it is a key reactive in many cases. Commercial
intumescent coatings, when fully expanded, often show a white exterior
of the expanded foam, even though the inner part near the substrate is
dark carbonized material. This white exterior has been identified
analytically [85] as mainly titanium pyrophosphate, formed by the
reaction of APP (probably \textit{via} phosphoric acids) with \textit{TiO}_2. Another
authority [86] proposes that titanium pyrophosphate is formed by
reaction of \textit{P}_2\text{O}_5 with \textit{TiO}_2 in the intumescing coating.

An early overview of intumescent fire barriers by a Monsanto
researcher, Ellard [87] emphasized the importance of formation of a
glassy outer barrier layer, preferably with a high reflectance, and the
role of inorganic oxides (Ti, Zr, and Sb) and phosphates in producing
such a layer.
Intumescent Silicate Coatings

Water-soluble silicates have a long history of use as wood coating and impregnants. Because of their water content, and ability to melt, they tend to be fairly intumescent. They can be produced as intumescent powders and formulated in a binder for use as metal-protective coatings. An improved product of this sort with an intumescent temperature above 195°C, suitable for coatings or firestops uses a lithium–sodium–potassium silicate composition [88]. Another improvement on the alkali silicate coating is the incorporation of up to 5% sodium phosphate which allows for improved high temperature resistance such as at 905°C as needed in fuel fires [89]. Encouraging results were obtained with an intumescent inorganic silicate coating applied on a glass-reinforced polyester with a glass mat as intermediate layer; the ASTM E162 test for surface flammability was passed as well as a US Navy quarter-scale flashover test [90].

An intumescent powder blend was patented by Alcoa [91] comprising a fibrous (preferably vitreous) calcium magnesium silicate, used in a coating or mastic with a binder such as an acrylic resin or polyvinyl acetate.

An intumescent caulk or firestop can be prepared using 3M’s Expantrol® 4BW, a hydrated sodium silicate–borate in a formulation containing an acrylate–vinyl acetate–ethylene terpolymer, an organic phosphate plasticizer, zinc borate, a polyol and glass fiber [92].

Patents on Improvements in Intumescent Coatings by Boron-Containing Additives

An early patent [93] on epoxy-based intumescent coatings for wood or steel beams uses a melamine phosphate combination with melamine borate (optimum 7:3) to extend the protective time in a fire.

A fire-protective intumescent coating for steel is claimed [94] using a water-soluble sodium silicate, borax, ATH, and kaolin. Formation of a vitreous thermal barrier is shown to occur.

Boric acid is a component of a complex epoxy mastic [95] which also contains APP, a triaryl phosphate, THEIC, silica, perlite, and ceramic fibers. This was commercialized as a coating for protection of steel from hydrocarbon fires.

A French research group [96] showed that including boric acid in an APP–epoxy-based intumescent coating on steel gave not only longer thermal protection (highest expansion) but also better adhesion and better mechanical resistance. Reaction of the boric acid with the phosphate to form a borophosphate was shown [97].
Zinc borate, or at least a combination of zinc oxide and a borate, is claimed to improve the thermal protection of steel provided by an intumescent coating which contains the usual APP and melamine, in a rather flexible cured epoxy matrix [98]. An overview of the applications and performance of these polypropylene glycol (PPG) coatings on steel, particularly for offshore oil platforms, has been published [99].

**Patents on Improvements in Intumescent Coatings by Other Inorganic Additives**

Intumescent coatings based on the APP-char former–blowing agent–glass fiber combinations are made more protective at high temperatures by inclusion of Ti or Zr or other metal borides, nitrides, or carbides [100].

Refractory fibers, such as alumina- or silica-based fibers, are added to improve the high-temperature performance and long duration protection given by a complex intumescent formulation on wood or metal [101].

Intumescent coatings suitable for protecting steel against high-temperature (fuel) fires are enhanced by inclusion of sodium potassium aluminum silicate (nepheline syenite) or potassium aluminum silicate [102]. Synthetic glasses have been shown to enhance intumescent coatings [103].

A university study [104] compared a number of commercially available high-temperature ceramic fibers and some minerals incorporated into an epoxy and a water-based intumescent systems. Carborundum’s Fiberfrax® HS-70C (an alumina–silica fiber with other components) and Zicar® ALBF-1 (an alumina fiber) were found to enhance the toughness of the residual char.

Much effort has been expended on improving fire-resistant coatings by addition of nanoclays and other nano-dimensional inorganic fillers. A brief review of fire-retardant nanocomposite coatings by Koo and Pilato [105] is in a 2006 book. A study on wood-protective intumescent coatings at the National Institute of Standards joint with Polish researchers [106] showed that the level of flame-retardant additive needed in a butyl acrylate based formulation could be reduced by incorporating some organically modified montmorillonite clay, while maintaining fire properties as determined by cone calorimeter. Studies in China [107] showed that adding up to 1.5% phyllosilicate clay or layered double hydroxides (both having layers of nanometer thickness) improved the thermal shielding by the char layer. In an overview by Turin Polytechnic investigators [108], nano-scale additives were proposed (with limited data, mainly on phyllosilicate clays) to give fire protection benefits in intumescent paints; additives specified were
montmorillonite, hectorite, saponite, double-layer MgAl hydroxides, zirconium phosphate, carbon nanotubes, nanosilica, nanotitania, nanoalumina, fullerenes, and silsesquioxanes. Exfoliated montmorillonite clay was shown by Hu and Koo [109] to have a synergistic effect in a conventional intumescent wood coating.

Chinese studies [110] showed that about 4% of nanometer silica or magnesium hydroxide, surface modified by Solsperse® 17000, can improve the water resistance of APP–pentaerythritol–melamine coatings without harming flame retardancy.

**Catalysts to Improve Intumescent Formulations**

The addition of certain spirobis amines (example: 2,4,8,10-tetraoxaspiro-5,5-undecane-3,9-dipropamine) and quaternary phase transfer catalysts (example: tetrabutylammonium salts) are shown to improve the performance of intumescent systems based on APP, melamine phosphate or ethylenediamine phosphate [111]. The working examples are in non-coating systems.

**Patents on Expandable Graphite in Intumescent Coatings**

Citations in recent patents provide a history of the use of heat-expandable acid-treated graphite flakes to boost the fire-barrier properties of various types of intumescent coatings. A representative patent by Huber inventors shows use of expandable graphite plus an acid-capturing additive such as calcium carbonate to enhance a typical intumescent system for wood [112]. The combined use of expandable graphite with glass or ceramic microballoons is shown in an otherwise-typical intumescent coating for building components such as steel conduits [113]. Another Avtec patent [114] shows use of expandable graphite together with a cement and a ceramic in a smoke- and fire-resistant coating with typical intumescent components. The use of expandable graphite in an acid-hardenable resin coating is shown for use on oriented strand board, fiberboard or glass-reinforced sandwich panels in a Georgia-Pacific Resins patent (2001) [115].

**Binders for Intumescent Coatings**

A variety of polymeric binders have been used. In water-based intumescent coatings, a polyvinyl acetate emulsion is often chosen, and it is believed to also contribute to the char.
In a comparison of various binders for a conventional APP–melamine–pentaerythritol formulation, chlorinated rubber blended with chloroparaffin gave high performance and withstood aging [116]. The use of a low modulus rubber with a similar intumescent formulation for steel coating has been claimed in a patent disclosure by British inventors [117].

In an Eliokem patent application [118], it is shown that a combination of a linear and a crosslinked (reticulated) methylstyrène–acrylic copolymer not only reduces flame spread in the early stages of a fire but also improves the char formation and insulating properties of the char in the later stages of a fire. Eliokem researchers [119] have discussed the systematic development of optimized substituted styrene–acrylate latexes for fire-resistant coatings. Better water resistance compared to vinyl acetate copolymers is shown. A study at Eliokem indicated optimum thermal stability of protective coatings for metals by combining 2-ethylhexyl acrylate-p-methylstyrène linear and reticulate copolymers [120,121]. The Eliokem styrene (or vinyltoluene)–acrylate copolymer resins, sold as Pliolites®, are used in Leighs Paints solvent-based intumescent coatings on steel, for example protecting the large steel structure of the Wimbledon tennis courts (2009 report). Studies at Eliokem have elucidated the relative efficiency of various thin film intumescent coatings [122].

A polymerizable resin approach is shown in a W. & J. Leigh patent [123] which discloses a classical APP–pentaerythritol–melamine intumescent formulation with a polymerizable acrylic resin plus preferably a preformed meth(acrylate) polymer plus a free-radical polymerization initiator such as benzoyl peroxide. This provides a liquid formulation which cures to a solid on a substrate such as steel. A related patent [124] uses a similar liquid composition with a reinforcement structure such as fiberglass or steel mesh.

Solid intumescent formulations suitable for powder coatings are described in a Leigh patent [125] and a wide variety of thermoplastic and thermosetting binders, including polyethylene, are said to be useful but the working examples use a thermoplastic polyetheramine, Dow Blox® 2100.

Improvement in adhesion of intumescent coatings to metal is claimed to result from including in an acrylic binder formulation a copolymerizable acid monomer, namely, an acid (meth)acrylate, maleic, fumaric, or itaconic acid [126].
Epoxy-Based Intumescent Coatings and Mastics for Steel Protection

Present-day formulations can be rather complex, particularly those used for their intumescent thick coatings (mastic) such as employed for protection of off-shore oil drilling platforms and petrochemical installations.

Examples of such advanced and proprietary formulations are Textron’s (now Akzo Nobel’s) Chartek® and PPG’s Pittchar®. An example of a Pittchar® formulation is disclosed in a PPG patent [127]. The formulation is as follows (component; parts by weight): Package 1: diglycidyl ether of bisphenol-A, 35.77; melamine, 2.75; APP, 4.52; tall oil fatty acid, 4.27; tris(2-chloroethyl) phosphate, 8.79; attapulgite gellant, 3.31; boric acid 20.64; zinc borate, 7.87; wollastonite, 12.05. Package 2: Versamid® 150 curing agent, 72.25; Aerosil® vapor-phase-produced silica, 3.50; Limsil® A-10 silica, 13.72; attapulgite gellant, 4.50; talc, 6.00. Packages 1 and 2 are mixed in 1.65 weight ratio before applying. This coating is applied in a thick layer as a mastic. A more flexible epoxy coating with many of the same ingredients but with a polyester-chain-extended epoxy has been described in later PPG patents [128,129].

An interesting intumescent coating for steel has recently been patented and probably commercialized by Chance & Hunt Ltd and Ferro Ltd [130], wherein a combination of an epoxy resin with an aldehyde resin or ketone thermoplastic resin serving as part of the binder and as the ‘carbonific’ (char-forming) component. The formulation is: 18% epoxy resin, 6% phenolic curing agent, 10% ketone resin (such as BASF’s Laropal® A81), 3.5% % hydrogenated castor oil viscosity modifier (such as Rheox’s Thixcin®), 55% APP (such as Exolit® 422), and 7.5% TiO₂.

A low-density epoxy-based intumescent coating, Chartek® VII, is described in a Textron patent [131]. The composition, which must be mixed in a very specific sequence and manner, is quite complex, as presented in Table 1. Each of the two parts is mixed before applying: by spray equipment

The density of this coating can be further reduced by pressurizing and dispersing a gas in it before applying. This recipe suggests that sophisticated formulation development is needed to achieve competitive products in the flame-retardant coatings field.

Recent intumescent coatings with lengthened fire resistance have made use of the very active dialkylphosphinate aluminum salt as part of the flame-retardant composition [132]. A representative formulation used 25 parts of boric acid, 9 parts of THEIC, 2 parts of TiO₂, and 5 parts
of a mixture of APP and aluminum diethylphosphinate (Exolit® OP1230) in 100 parts of epoxy resin (Beckopox® EP140) cured with an aliphatic polyamine. Cured on steel at 3.5 mm, this coating gave 44 min of fire resistance.

**Special Applications of Intumescent Coatings**

Multi-layered structures can be used to give a high degree of fire protection to steel structural elements; one patent [133] indicates that an outer layer can be fiberglass with an intumescent coating, on top of a reflective metal foil, on top of a low conductivity refractory-fiber blanket, on top of another reflective metal foil layer. A similar multi-layer construction can be used to protect conduits and cables [134]. The No Fire technology also has found application in passenger aircraft.

The multi-layer concept was applied differently in a patent to Battelle inventors [135]. Here, the idea is to apply a first intumescent coating layer on the substrate, then on top of that, another intumescent coating which forms a less dense layer of foam when exposed to fire, the outer
layer giving the immediate fire protection and the inner harder layer providing a second layer of defense in case breakthrough of the outer intumesced layer occurs. The outer layer formulation is based on APP, dipentaerythritol, and epoxy with an azobiscarbonamide blowing agent.

The use of intumescent coatings on plastics, such as plastic pipe, is disclosed in a Monsanto Europe patent [136]. These coatings, however, are not paints or mastics but appear to be extruded or laminated, and have a substantial thermoplastic, possibly foamed thermoplastic, content.

Thin intumescent coatings on wire and cable, applied by melt extrusion, are described in a patent application of Reyes [137] using formulations in a polyolefin including melamine phosphate, ethylenediamine phosphate, and activators of the pentaerythritol spirobisacetal, and quaternary ammonium types as mentioned earlier in connection with a Rhodes et al. [111] patent.

Polyurethane foams used in thermal insulation can be made fire-resistant by an intumescent coating, preferably applied by spraying, as described in a patent application [138]. Another coating for the same purpose is a water-based Flame Seal®-TB Spray-Applied Thermal Barrier from Specialty Products, Inc. [139]. Further foamed coatings applicable to thermal insulation for fire, sound, and heat barriers are described by Lanxess [140].

Patented combinations of intumescent paints (such as based on APP, pentaerythritol and melamine, and latex binder) with mold inhibitors and insecticides (particularly termiticides) have been disclosed [141,142]. These may be applied to any substrate for fire, mold, and insect (termite) protection.

**Intumescent Coatings on Textiles**

These coatings are usually applied to the surface as a layer. Products from Thor (France) used in this way are Aflamman® PCS and Aflamman® IST (water-soluble organic–inorganic phosphorus nitrogen combination), applied with a polyvinyl acetate emulsion binder Rhenappret® RA. A French study shows that this finish on polyester fabric lengthens the time to ignition and shortens the time to extinction, and can provide a French M1 (non-flammable) rating [143].

Improved fire-protective performance on substrates such as, particularly, textiles is claimed for intumescent coating formulations containing APP, pentaerythritol, and melamine with specific latex polymers (styrene–acrylate–methylenebisacrylamide copolymers exemplified) having a thermogravimetric weight loss of at least 7% at 370°C [144].
Improved thermal and warm water resistance properties of coated textiles such as car interior fabrics are said to be achieved by use, in place of APP, of a melamine phosphate coated with a functional organosilicon resin [145]. An extensive university study of phosphorus-containing flame retardants in backcoating of textiles was conducted in the UK [146]. These formulations are not necessarily intumescent ones.

**Silicone Coatings**

Silicone coatings with dispersed carbon nanotubes have been introduced as Nanocyl’s ThermoCyl® to give fire protection to a wide variety of substrates, such as plastics, cables, textiles, foams, metals, and wood [147]. Coatings as thin as 100 μm have been shown effective. These do not appear to be intumescent coatings.

**Very High-Temperature Ceramic Coatings**

Coatings such as Al₂O₃–TiO₂, ZrO₂, and other ceramic thermal barrier coatings are used, for example in aerospace, electronic and biomedical applications, and may be applied usually to metal substrates by plasma/high-velocity oxygen flame spraying. Further discussion is outside the scope of this review and the reader is directed to the annual proceedings of the International Thermal Spray Conference. Slurry methods of application of ceramic coatings are also used to provide metals with short-term exposure to high temperatures, and have been reviewed [148].

Aerospace tiles, which are inherently fire resistant, can be coated with further heat-resistant coatings such as a recently disclosed system of ceramic/metal nanoparticles [149].

Ceramicizable compositions, suitable for cable coatings and seals, have been developed by an Australian group [150] on the basis of a silicone polymer, mica, and a combination of a low melting glass and a high melting glass. These inorganic materials flux to form a self-supporting protective ceramic coating after the organic component has burned away. The same research group discloses a related ceramifying coating material, suitable for protecting cables at high temperature, using an inorganic phosphate, which is exemplified by APP, as part of the ceramifying system along with a mineral silicate exemplified by talc, mica, or clay [151]. A discussion of the science and technology of this approach has been published by the Australian researchers [152].

Australian researchers [153] described a basic study which led to ceramifying compositions based on polyvinyl acetate, kaolin or talc,
magnesium hydroxide, and zinc borate (as flux). Kaolin provided stronger ceramic but talc provided a better thermal barrier for firestop applications.

**Intumescent Coatings on Reinforced Thermoset Composites**

An extensive study of intumescent coatings for shipboard use, using small-scale and full-scale fire, adhesion and impact tests, by the US Navy [154] showed failure to meet Navy criteria when used as stand-alone coatings on reinforced thermoset composites. Many of the coatings demonstrated poor adhesion during fire tests. However, some did reduce flame spread and smoke generation when applied over reinforced plastic, and one which contained a mineral adjuvant performed well in combination with StructoGard\textsuperscript{®} (a mineral blanket).

**Testing of Fire-Protection Coatings**

A succinct review of tests for fire-protective coatings, especially for steel, is found in a 2002 BCC paper [155].

Typical large-scale tests in the USA are the ASTM E-84 (Steiner tunnel) for flame spread and the ASTM E119 for fire resistance. There are also UL 1709 or ASTM E1529 for protection time in a rapid temperature rise fire, such as the one which may occur in an offshore oil or gas platform. Both UL 1709 and ASTM E1529 require a test furnace which develops an average temperature of 2000°F (1093°C) in the first 5 min. The principal difference is that the UL 1709 involves a total heat flux somewhat larger than that in ASTM E1529. These are all quite large tests with specially dedicated equipment. The test method, ASTM E119 (also UL 263 and the similar ISO 834 used elsewhere in the world), involves a large test rig, has been used for decades and is still used to measure the fire performance in a solid fuel fire (‘cellulosic’ type fire), of walls, doors and floors. For combustible construction materials such as wood, the ASTM E-84 is commonly used to measure the effectiveness of coatings to retard flame spread. However, this test requires large samples and is relatively costly. A useful ability to predict E-84 results on coated wood was demonstrated using small-scale tests in the cone calorimeter Koo’s group [156].

Standards and tests relating to civilian shipboard fire protection are under the SOLAS Codes of the International Maritime Organization and in the USA, administered by the Coast Guard. An overview of the standards going into effect in 2003, and systems for meeting these standards, was presented in 2002 [157].
From a research standpoint, a faster and convenient small-scale screening test was developed at Lille [158]. This test involves using a small radiant heater (the French epiradiateur, directed downward on a $5 \times 5 \text{ cm}^2$ plate painted with the test coating. An infrared thermometer is used to read the bottom temperature of the plate. Even more informal tests of this sort are sometimes run for purposes of formulation development, using a propane torch held at a fixed distance from the coated plate.

British standards for fire-protective coatings are discussed and illustrated in a 1983 review which covers in special detail the railway requirements and experience [159]. A major standard for fire protection of building materials has been BS 476, part 21. This has been replaced by the CEN standards of the European Union and the related ISO 834 standard elsewhere.

**Firestops**

In a building, penetrations through fire-rated walls and floors/ceilings for pipes, ducts, cables, wires, conduits, and structural members provide dangerous pathways for fires and fire gases to spread. In recent years, building officials and fire marshals have begun to prioritize firestopping barriers in building codes. In the USA, fire-stopping should use products tested and approved under ASTM E 814, a test with a specified flame at one side of the aperture, and means for measuring temperature on the other side. Time for no passage and time to reach 400F are measured, as well as air leakage. Resistance to a hose stream is also evaluated.

Much of the patent literature on firestops emphasizes the mechanical aspects such as shaping to fit various apertures, the use of shields and supports, putty-like materials, and combinations with aperture blocking means such as mineral wool. We will cite some representative patents of leading firestop manufacturers which emphasize the compositional aspects, often complex, and often proprietary.

A flexible felt containing an intumescent material was patented by 3M [160], the composition comprising an acrylic latex, a phosphate plasticizer, an APP, an acid-treated expandable graphite, ATH, sodium aluminate, aluminum sulfate, and various surfactants applied to a mix of ceramic fibers and rayon fibers, and compressed to a fire-barrier felt.

A more recent solid fire sealing material patented by 3M [161] comprises a dried rubber latex, TiO$_2$, APP, a phosphate plasticizer, 3M’s Expantrol® (a granulated hydrated sodium silicate), and various stabilizers. A firestop putty, also patented by 3M [162] contains a mix
of rubbers, epoxy resin powder, silica, melamine, boron oxide, fiberglass, a liquid olefin copolymer, and Expantrol® or expandable graphite.

A version of expandable graphite said to be advantageous as a firestop ingredient because of reduced onset temperature and higher expansion is patented by Hilti [163] and it uses nitroalkane and ferric chloride for intercalation of the graphite. Another Hilti patent [164] describes a complex formulation for a two-component intumescing foam comprising specific polyurethane foam-forming ingredients, APP, tris(chloroisopropyl) phosphate, dipentaerythritol, melamine cyanurate, zinc borate, iron oxide, silica, expandable graphite, and urethane catalysts; this formulation is injectable into wall apertures as a firestop.

Flexible intumescent sheets, suitable for firestops in the gap between door and doorframe, were patented by Rectorseal [165] which comprise expandable graphite, ethylenediamine phosphate (an intumescing salt), and a soft emulsion resin.

A two-stage expandable firestop was patented by Specified Technologies [166] which makes use of a two-stage expansion: the lower temperature expansion uses microcapsules with polyvinylidene chloride walls filled with liquid isobutene and the higher temperature expansion uses expandable graphite, both in an acrylic latex. A related firestop system [167] uses expandable graphite plus alkane-filled microcapsules (Akzo-Nobel Expancel®) or a nitrogen- or CO₂-releasing blowing agent, plus, as a supplemental flame retardant, a phosphate, borate, or clay.

**FLAME-RETARDANT GELCOATS**

These are coatings made from curable unsaturated polyester resins and cured in place, typically onto a glass-reinforced polyester laminate. They are often in the range 0.4–0.5 mm, and provide a smooth surface to the laminate. Unlike paints, they may be applied as an early stage of laminate production, such as in the mold. Typical formulations are similar to regular unsaturated polyester resins, and with similar curing catalysts (usually peroxides) but with thixotropic agents added to control rheology. Flame retardancy requirements for gelcoated composites are often found in railway, construction, and marine applications. A new railway requirement in Europe is the EN 45545 standard which involves a flame spread test, as discussed in a recent Cytec paper [168]. Intumescent formulations such as based on APP, pentaerythritol and melamine may be used. ATH may also be used but high loadings have viscosity problems. A UK article [169] discusses the trade-off between
weatherability and flame spread, and the choice of putting the flame retardant in the gelcoat or in the base laminate. A recent article from Clariant [170] shows that the British rail standard 476 can be passed by using 50 phr of Exolit® AP 740 (an APP plus a char former) in a gelcoat plus 50 phr ATH in the laminate or 100 phr Exolit® AP 740 in the gelcoat and none in the laminate. This second option is especially useful for the resin transfer molding process.

**CONCLUSIONS AND FUTURE DEVELOPMENTS**

Effective products have evolved to meet fire protection requirements on steel, wood, and to some extent on plastic or elastomer substrates. Depending on composition and thickness, protection can be offered against both lower energy ‘cellulosic’ fires and high-energy ‘hydro-carbon’ fires.

Demanding new standards for fire testing, test standardization, and product classification, such as ENV 13381 and EN 13501 may drive the development of improved intumescent and other types of fire-protective coatings, predicted by European coatings workers [171]. In the USA, wider adoption of the ICC building codes continues, and some of the requirements can be met most economically by fire-resistant coatings. Environmental considerations, particularly strict solvent limitations to limit air pollution, strongly favor water-based or high-solid coatings.

Some shortcomings still need to be met by further research and development. Weathering of exterior intumescent coatings has usually been inadequate because of hydrophilic components. Protective top coatings can be used, but add to cost. A recent patent application claims that the inclusion of a highly water-resistant resin component, exemplified by a polyvinylidene fluoride emulsion such as Arkema’s Kynar® Aquatec, in an otherwise typically hydrophilic intumescent formulation improves water resistance [172] and may avoid the need for a protective topcoat.

Adhesion of fire-resistive coatings to substrates, particularly steel, may require a primer coat, but this also may be avoidable by self-priming formulations. Adhesion to plastic or elastomer surfaces presents an R&D opportunity. Single coating applications have obvious cost advantages.

A shortcoming of some protective intumescent coatings on steel columns is the tendency to crack open at the full extent of their expansion, thus exposing the substrate to the flames. A recent patent application by a Japanese company (2010) [173] indicates an
APP–pentaerythritol–melamine formulation in which the cracking propensity has been controlled by including rockwool fibers.

REFERENCES


BIOGRAPHY

Edward D. Weil

Dr. Weil received his BS degree in chemistry from University of Pennsylvania in 1950 and his PhD degree in organic (polymer) chemistry from University of Illinois in 1953. He conducted and managed research in industry (Hooker Chemical Co., Stauffer Chemical Co.) for 33 years and has served as Research Professor at Polytechnic University (now Polytechnic Institute of NYU) since 1987. His industrial and academic research has covered a wide variety of flame retardancy topics, has led to many patents and several commercial flame retardants and he consults actively in this field. He has authored many papers and encyclopedia articles in flame retardants, phosphorus, chlorine and sulfur chemistry. The present review supplements his co-authored book (2009) on flame retardants for plastics and textiles.