Advances in Intumescent Technology

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Since 9/11 there has been renewed interest in improving the fire safety of buildings. This movement applies not only to the physical structure of the building but to the building’s furnishings and decorative elements as well. Although active fire suppression systems such as sprinklers and fire extinguishers continue to be employed, fire code officials increasingly believe that passive systems are needed as well to reduce smoke and slow fire spread. These passive systems require materials that are either innately fire proof or that can be protected by the incorporation of a fire retardant into the material or by coating the material with a fire retardant coating. This paper will address intumescent technology for the production of fire retardant coatings and discuss both the theory and technology for formulating intumescent coatings.

To start, the term intumescent when applied to fire protective coatings refers to a technology wherein the coating will swell and form a multi-layered char foam when exposed to heat. High carbon containing chars are extremely heat resistant and are employed in critical high temperature applications such as the carbon on carbon composites that are machined to produce rocket exhaust nozzles. The production of these carbon on carbon composites involves the combination of graphite fibers with high char yield epoxies. After cure these parts are graphitized in a high-pressure autoclave at high temperatures. These parts are then thermally stable to above 1000 C. The same principles apply to intumescent coatings where in, with the right choice of materials, a low thermal conductivity char foam can be created out of a coating.

Before reviewing the chemistry of intumescence let’s make a wish list for a fire retardant coating.

The ideal fire retardant coating should:

1. Have low flame spread
2. Have low smoke toxicity
3. Provide thermal insulation protection
4. Provide long term protection from heat and flame.
5. Not produce a lot of smoke
6. Be easy to apply
7. Be cost effective
8. Have good wear resistance
9. Adhere to the underlying substrate
10. Be flexible or hard, as the application requires
11. Not use hazardous materials that will compromise green and cradle to cradle certification
12. Etc., etc.

Just as this wish list can become quite lengthy so can the possible applications for such a coating. To name but a few; the protection of structural steel, the protection of foam insulation including urethane, polypropylene and polystyrene, the protection of fabrics used for draperies and upholstery and the protection of fiberglass tanks and infrastructure.

Intumescent has been used commercially since the early days of space exploration for the heat shield of the re-entry vehicles and in the protection of off shore oilrigs since the tragic Piper Alpha 3 disaster. Intumescent incorporates an ablative burning mechanism wherein heat is consumed via an endothermic char forming reaction while the thermally stable char seals in hot gasses with near zero mass. The char ideally blocks out heat transfer via conduction, convection and radiation. Although all of the Apollo series re-entry modules used a heat shield that worked, (if you saw the movie Apollo 13, even better than expected), NASA, mistakenly used the now infamous silicone tiles on the Shuttle. For all you space buffs I am pleased to say that the Orion craft that will succeed the Shuttle will once again use an
ablative/intumescent heat shield. And, for all the epoxy formulators, you will be pleased to know that both the Apollo and Orion series heat shields are based on epoxies.

The chemistry of char formation is a classic dehydration reaction between hydroxyls, carboxylic acids and amines or amine groups to form polymeric linkages. The dehydration reaction requires heat and is enhanced by an acid catalyst. Water and ammonia are liberated during these reactions. Some materials contain oxygen or nitrogen on every carbon and have a natural propensity for char formation. An example is starches and sugars. If you ever toasted a piece of bread a little too long or toasted a marshmallow over a fire you have experienced char formation. Classic intumescent agents are amino phosphates or amino sulfonates that, upon heating, liberate phosphoric or sulfonic acid to catalyze the dehydration reaction and ammonium ions to facilitate char formation. The problem arises when you have an aliphatic carbon chain as part of your polymer. These portions of the polymer have little ability to form char. For example, a straight chain hydrocarbon such as butane will burn cleanly with near zero char produced. This burning mechanism involves several steps. First hydrogen is removed with heat and quickly reacts with oxygen to produce water and heat. The resulting hydrocarbon, partially stripped of its hydrogen atoms now has double bonds. Further heating will cause these bonds to break allowing carbon atoms to be oxidized to produce carbon dioxide and carbon monoxide. The oxidation of carbon is even more exothermic than the oxidation of hydrogen and if the carbon chains begin to break a far greater amount of heat will be released. Alternatively there may be a catalytic approach to add oxygen across double bonds before the carbon – carbon bonds break. This is commercially done in the production of maleic anhydride from butane. In the production of maleic anhydride the butane is heated during a dehydration step to remove hydrogen but not enough to break the carbon – carbon bonds. Then, in the presence of a catalyst, oxygen is added to form maleic anhydride, C4 H10 goes to C4 H2 O3. One company has patented the combination of conventional amino phosphate technology and a technology for adding oxygen to hydrocarbon chains to produce a new class of patented intumescent agents trade named Intumax. These new intumescent agents allow the use of less intumescent agent in formulations, which, in turn, greatly improves the physical and adhesive properties of the coatings.

To best formulate intumescent coatings several additional chemistry considerations must be considered. From the above discussion it can be deduced that the more oxygen and nitrogen on carbon the easier it will be to produce a char. In addition the more double bonds the less heat will be released during the initial burning stage. Also, the temperatures at which dehydration and de-hydrogenation reactions occur vary for different polymers. The choice of intumescent agent must be done carefully so that the release of acid catalyst, oxygen addition catalyst and recombinant ammonium ions occurs simultaneously with the dehydrogenation and dehydration reactions.

Other considerations involve the melt flow rheology, the char height and char strength. There are also the conventional formulation considerations having to do with everything from thixotropic behavior to flexibility and everything in between. When formulating intumescent coatings try to make intelligent choices that help char properties not hurt them. For example, since char layers have to remain on the surface wetting agents and defoamers that reduce surface tension should be avoided. Certain fillers can have synergistic benefits. Ceramic and phenolic micro spheres add to the thermal insulative properties. TiO2 and other metal oxides add to the char strength. And pentaerythritol and melamine have a high propensity for char formation.

To best understand how these considerations come into play lets look at several case studies.

Disclaimer: The formulations presented here are simplified for the purpose of education and the test data presented are for systems similar to these but not for these specific formulations.

1. A steel coating to protect structural steel for up to 2 hours according to E 119 test protocol:

Considerations:

Good adhesion to steel, hard, gray in color, sprayable, able to build thick coating of 0.5 inches with no sag or drip, able to cure in 24 hours at 50 F, work time greater than 1 hour.
Resin choice: Bis A/Novolac mixture chosen for viscosity and cure temp requirements as well as low smoke and good thermal stability:

Curing agent: TETA, Chosen for cure speed and low level of aliphatic hydrocarbon chain.

Diluent: P-tertiary butyl phenyl glycidyl ether, Chosen for viscosity reduction and heat resistance and char forming properties.

Intumescent agent: Intumax AC-2, Chosen for activation temperature i.e. approx. 300 C. Highly effective low loading level required.

Additional char forming additives: Melamine and Pentaerythritol: Chosen for high levels of hydroxyl amine availability.

Thickeners: Mineral wool and kevlar pulp. Chosen for thixotropic ability.

Additional fillers: Phenolic micro spheres, Chosen for low thermal conductivity.

Pigment: Expandable graphite, Chosen for swelling properties and pigmenting ability.

Formulation:

**PART A**

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<td>DEN</td>
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<td>DER</td>
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<tr>
<td>PHEN. MICRO SPH.</td>
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<tr>
<td>INTUMAX AC-2</td>
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<tr>
<td>KEVLAR PULP</td>
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<td>MINERAL WOOL</td>
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**PART B**

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**MIX RATIO A:B** 100:20

**PROPERTIES**

- Gel time 200 gm mass at 25 C 2.5 hours
- Gel time 200 gm mass at 15 C 5 hours
- Sag at 0.5 inch thickness along vertical surface - less than 0.2 inches
- Flame spread E 84 less than 2 feet
- Smoke density E 84 less than 100
- Steel beam heat time E 119 0.2 inches over 1 hour
  0.5 inches approx. 2 hours
2. A flexible water based coating for drapery blinds required to pass E-84 flame spread class A requirements and have near zero smoke generation.

Considerations: Must be flexible, low cost, 1 component and be able to be thinned with water. Must also be permanent.

Resin choice: Styrene acrylic that has a low Tg and is self cross linking.

Intumescent additive: Intumax AC-3WM for low activation temperature, neutral pH and char forming ability.

Thickeners: Hydroxy ethyl cellulose, char forming abilities and effectiveness in water based systems

Additives: TiO2 for char strength and light blocking ability, Melamine for char formation.

Formulation:

Styrene acrylic with Tg of –15 C (60% solids) 50
AC 3 WM 34
Water 10
HEC 0.5
TiO2 3.0
Melamine 2.5

Properties

Flexible and non-cracking even at 0 C. Can be thinned with water. Effective on cotton, nylon and polyester fabrics. Achieves UL 94 V0 rating on all of the above and on cotton fabric achieves a rating of less than 5 on the smoke index and a class A flame spread applied at a level of 100 grams per square yard.

3. A thin semi flexible epoxy for coating foam insulation and composite parts. Must have expansion of 100 times film thickness.

Considerations: Must have long working life and be able to cure to tack free in 24 hours at 25 C and 60% RH.

Resin choice: Bis A epoxy for cost and char forming properties.

Curing agent: A flexible amine/polyamide with accelerators.

Intumescent agent. Intumax AC-2/ Intumax AC-3 blend to achieve effectiveness over the widest range of decomposition temperatures.

Fillers: TiO2 for char strength, wollastonite for strength and hydrated alumina for added fire retardancy.

Diluent : t-butyl phenyl glycidyl ether and phophte ester for char formation and heat resistance.

Formulation:

Part A PBW
DER 331 42
t-BPGE 6
Phosphate ester 12
Intumax AC-2 18
Intumax AC-3 6
TiO2 5
ATH 10
Wolastonite 1

Part B

Jeffamine D-400 14.5
Ancamine 1608 3.0
Ancamide 350A 1.5
Accelerator 399 2.0

Mix ratio 100:21

Properties: Can be applied as a thin coating 5 mil thick via airless spray gun without dripping. 5 mil thick coating expands to over 0.5 inches upon heating above 300 C. Flexible, Shore D hardness 70. Working time 8 hours. Tack free 48 hours at 60% RH. Passes class A smoke and flame spread requirements and passes the first 15 minutes of the E119 test for foam insulation protection.

Conclusion: The market for fire retardant, halogen free coatings is rapidly expanding. Intumescent technology is the best alternative for meeting the requirements of the niche markets that are emerging. By understanding the chemistry of intumescence and by utilizing the new intumescent additives now available the formulator can formulate systems to meet these arising challenges. Good luck to you all.