

A look at the global market for high heat resistant coating systems. The second of a two-part series.

High heat resistant coating systems

In the April issue of *Coatings World* we discussed Heat Resistant Coatings (HRC) applications; the importance of pigmentation and the market size and growth rates. We separated the applications by cure mechanisms, resin species, number of coats and filler types. We also segmented the regional share of market into four with NAFTA being the largest followed by Europe, China and South America and the types of coatings, with liquid occupying 86% and powder the remaining 14% of the global market for HRC's.

FOUR TYPES OF HRCs

The salamander is a type of lizard that is said in mythology to have been able to live in fire, cooling itself with its breath. Coatings which achieve similar effects are more reliable, and are found in several related yet distinct applications:

- High-build surface insulation coatings for industrial use and to improve the thermal efficiency of older buildings;
- Heat-reflecting (using IR-reflective pigments, not necessarily high-build) coatings, particularly useful for roofing systems in hot climates;
- Coatings resistant to high temperatures during service; and
- Coatings which retard the spread of fire or minimize fire-related damage to structures.

For this article, we are concerned with the technologies used in the last system only.

FIRE-RETARDANT COATINGS

High-temperature coatings are required to protect metal surfaces such as barbecues, cookers, non-stick cookware, engine components, boilers, vehicle exhausts and even the working parts of rockets from oxidation over an extended period. These materials are usually liquid coatings, but powder coatings have also been developed which will resist tempera-

tures above 450°C, sufficient for most of the applications listed above.

Fire-retardant coatings, on the other hand, are the latent 'emergency response systems' of the coatings world. With luck, in most applications, their performance will never be tested and they will simply have to function as decorative, protective or anticorrosive finishes. They may or may not encounter high temperatures during normal service. Some, indeed, cannot tolerate high service temperatures, since their protective action depends upon controlled degradation in fire situations.

All types of surfaces may require protection against damage by fire, most obviously wood and steel. It is not possible for coatings to provide indefinite protection against severe fires, but delaying the spread of fire, or maintaining the integrity of a structure against fire for periods of 30 minutes to four hours is possible. That greatly increases the time people have to escape and gives firefighters more opportunity to limit the extent of damage.

The application areas are generally either industrial or institutional, for example:

- Protecting people, in fire escape routes in large buildings;
- Protection of structural steelwork against collapse, interiors of ships; and
- Manufacturing plants in the chemical industry and other high fire risk businesses.

It has been noted that the flammability of ordinary decorative coatings can be quite low, simply because the high levels of inert filler retard combustion of the binder system. However, where some form of 'active' fire protection is sought, a number of distinct approaches can be used, alone or in combination, to increase the levels of substrate protection that a coating provides.

The main underlying mechanisms are:

- To slow down the spread of fire by diluting

oxygen with non-combustible gases, which will also absorb some of the heat;

- To lower combustion temperatures by endothermic reactions. As an example, the liberation of water of crystallization and its conversion into steam involves both of these processes;
- To interfere with the free radical reactions which occur during combustion;
- To produce a protective, impervious surface layer; and
- To insulate the underlying substrate from temperature rises.

Although all organic polymers are intrinsically flammable, the way in which they undergo thermal decomposition has a major bearing on their fire resistance. A major focus of research is the extent to which carbonaceous char is formed. Pure carbon is technically flammable, but not necessarily easy to ignite (as barbecue users may already recognize) and polymers which degrade to a carbon char rather than burning cleanly in a single process will slow down the spread of flame, contribute less heat to the combustion process and provide a degree of protection to the substrate.

It has been shown, for example, that bisphenol C has a much higher char yield than the bisphenol A more commonly used in epoxies. There is some evidence that this difference is due to the formation of diphenylacetylenes during thermal decomposition of bisphenol C, and it has also been shown that poly(aryletherketone) containing diphenylacetylenes has a heat release and char yield similar to that of bisphenol C, suggesting that polymers using other curing systems but degrading in a similar fashion could be formulated to give a high char yield too.

Many fillers containing halogens, phosphorus, antimony or boron have been widely used for their fire-retardant properties, both in coatings and as plastics additives. Halogens and antimony in particular have the considerable disadvantages of producing toxic gases upon combustion

and environmental pollution upon disposal.

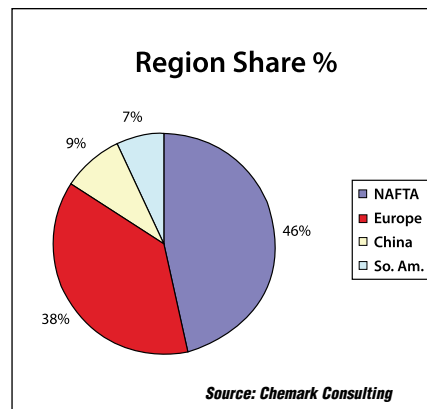
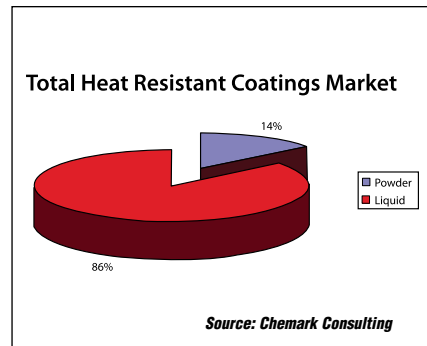
Pure PVC, containing 57% chlorine by weight, will not catch fire. But its melting point is too high and its solubility too low for practical application in coatings, and it produces toxic smoke at high temperatures. Chlorinated alkyds and chlorinated paraffins have been used as binders and plasticizers, but their use is being restricted or banned on environmental grounds. Thus, alternatives are being sought for many of these materials.

An important consideration is that different flame-retardants operate through different mechanisms, and the inclusion of materials with more than one protective mechanism will generally be more effective than relying on related compounds with similar features.

For example:

- Halogen-containing compounds block the free radical processes, which take place during combustion. Some other compounds have similar effects;
- Antimony compounds have a synergistic effect with halogens, probably by forming antimony halide compounds, which assist in carrying the halogen atoms into the gas phase;
- Phosphorus-containing compounds operate through the formation of glassy surface barrier layers or the promotion of charring, in either case producing a protective layer; and
- Zinc borate promotes char formation and is effective on its own, but is reported to have synergistic effects when combined with aluminum or magnesium hydroxides. It can indeed be used as a surface coating applied to these fillers.

Metal hydroxides, and in particular aluminum trihydroxide, are widely used as fire-retardant fillers. Their decomposition liberates water vapor and leaves non-combustible metal oxide particles, which remain attached to the substrate. Magnesium hydroxide is also effective, but has a higher decomposition temperature than aluminum hydroxide. Similarly,



calcium sulphate releases water upon combustion.

High-build coatings containing magnesium oxychloride can protect steelwork (though not wood) since the compound liberates large volumes of water upon heating to temperatures in the region of 500°C (900°F), where steel starts to lose its strength, but wood will already have caught fire.

OTHER COATING SYSTEMS

For maximum effectiveness, thick layers are required to insulate a flammable or degradable substrate from the heat of a fire. Cementitious coatings provide a means of protecting steel against fire. In this case, the requirement is to apply a very thick coating—three centimeters being generally required to give a two-hour fire resistance rating. For additional information regarding coatings, paints, adhesives, sealants and raw materials that find use in these value streams, contact Chemark at 910-692-2492 or visit them on the web at www.chemarkconsulting.net. **CW**

See Chemark's ad on page 27.