High performance in a nutshell

Cashew-derived curing agent excels in metal and concrete primers.
Jean-Luc Dallons.
Epoxy coatings are widely used as high-performance primers. Phenalkamines, derived from cashew nutshell liquid (CNSL) technology, is a sustainable technology as it uses a renewable raw material. A cashew nut contains about 20-25% by weight of CNSL [1]. This in turn has four main constituents: cardanol, cardol, anacardic acid and 6-methyl cardol. Cardanol is the basic chemical compound of CNSL. It can be used as a raw material for different chemicals such as polyamines, polyamides, polyamide adducts or Mannich bases. The main drawbacks of these technologies are:
- relatively slow curing speed when polyamides are used;
- blushing and toxicity when polyamides are used;
- toxicity, due to free phenol, when Mannich bases are used.

Epoxy curing agents need to suit the application
To protect metallic substrates, formulators have usually chosen the polyamide family of products. When concrete is to be protected, amines (e.g., isophorone diamine adduct), polyamide adducts or Mannich based are most often used. Epoxy coating technology is used in different market segments such as marine and offshore, general industrial and heavy duty, transport primers and concrete flooring. The requirements for marine, transportation and flooring coatings are discussed below and their main requirements are summarised in Table 1. It may also be noted that coatings performing well in the protection of ships are obviously good candidates for heavy-duty and general industrial protective coatings. New technologies are required to meet these demanding requirements, and phenalkamine curing agents are strong contenders.

Phenalkamine structure explains its properties
Phenalkamine curing agents are derived from cashew nutshell liquid (CNSL) technology. This is a sustainable technology as it uses a renewable raw material. A cashew nut contains about 20-25% by weight of CNSL [1]. This in turn has four main constituents: cardanol, cardol, anacardic acid and 6-methyl cardol. Cardanol is the basic chemical used to prepare phenalkamines, which result from polymerisation followed by amination. Cardanol, as shown in Figure 1, is a very interesting natural molecule that confers some specific valuable properties on coatings:
- The phenolic group acts as a catalyst for the curing of epoxy resins.
- Pendant -OH groups enhance adhesion either to the substrate or to the polyurethane topcoats most often used in these types of protective coatings.
- The aromatic ring confers chemical resistance on the coating.
- The aliphatic C15 chain, due to its apolar character, provides coatings with water repellence and thereby enhances anti-corrosion properties.
- Finally, this long aliphatic chain provides some flexibility to coatings. Thus, phenalkamines are excellent curing agents in coatings for ships and offshore constructions, metallic parts of commercial vehicles as well as concrete floorings. Their use is likely to be advantageous in other industry segments using protective coatings.

Cutting costs and corrosion in marine coatings
Marine coatings must protect metallic surfaces on ships against corrosion under extremely aggressive conditions. Today, marine coatings formulators are also challenged by environmental issues and the need to reduce costs without compromise on quality [2]. Shipyards must focus more and more on process costs rather than on the cost of raw materials such as paint [3].

The use of a universal primer or at least a reduction to two or three systems can save a lot of process costs, particularly if this is associated with a fast and all-season cure. Complexity can be reduced and productivity increased by standardising paint application procedures [3]. The introduction of double-hulled tankers, which provide an increased potential for corrosion, and are also changing the industry. Larger surfaces are exposed to corrosion, and maintenance is more difficult to handle and therefore more expensive. The need to protect the ships’ surfaces against corrosion at the original shipbuilding yard is therefore crucial [5]. Epoxy-phenalkamine primers show excellent anti-corrosion properties compared to conventional polyamide technology, as illustrated in Figure 2 which shows salt spray results after 750 hours exposure.

Phenalkamines cure epoxy resins quite quickly even at very low temperatures. This technology can be used all year round, as the pot life is long enough to allow the same primer to be applied in summer (see Figure 3).

Transport coatings: good adhesion to steel
The transport coatings industry will face stringent regulations regarding VOC emissions both in the EEC [6] and the USA [7]. Commercial vehicles are made up from different substrates and in most cases, the coating process is carried out after assembly of all the separate parts. The industry therefore requires good adhesion to be achieved on all these substrates.

To achieve good adhesion and corrosion protection on one of these substrates in particular, cold rolled steel (CRS), is rather difficult. A newly developed phenalkamine, while allowing formulations to be applied with less than 250 g/l VOC, provides excellent adhesion on CRS, even outperforming a benchmark coating with higher VOC content (see Figure 4).

Concrete can be coated before full drying
The coating of concrete requires many precautions in order to avoid problems of intercoat adhesion or osmotic blistering. The presence of water in freshly-laid concrete or in areas where it is applied below ground frequently constitutes a major problem for the contractor. It is also well understood that coating of concrete has to be carried out only after allowing 28 days for drying, and therefore becoming time-consuming. Failures could result in
exceptional costs and must be avoided as far as possible [8]. Because humans are often exposed, it is obvious that 100% solids systems are preferable. They may become the only technology in the future.

Some phenalkamines can cure epoxy liquid resins in the presence of a relatively high water content without any risk of blistering or of intercoat adhesion failure, for example when a PU topcoat is used [9].

Figure 5 shows that outstanding intercoat adhesion to a PU topcoat is achieved on a high performance concrete after only seven days of drying. The water content continues to decrease while the concrete’s compressive strength builds up, but the primer adhesion when applied after seven days is the same as after 28 days. The 100 % solid formulation also shows itself to be blister-free after performing the following test (Figure 6): a tile was first immersed in water, then the sides of the tile were coated and dried. The tile was once again immersed in water for one week before its upper surface was coated. The tile was then half-immersed in water and exposed to IR warming.

A cure for problems, not just coatings

Thus it can be seen that phenalkamines are excellent curing agents for epoxy resins and meet many of the future needs of protective coatings for marine, transportation, heavy duty and concrete industries. They provide both fast and low temperature curing, are surface tolerant and allow high-performance VOC-compliant coatings to be produced (Figure 7).

References
[9] J.L. Dallons, Middle East Coating Show, Dubai 2004

Results at a glance
- Phenalkamines, derived from cashew nutshell liquid (CNSL) can be used as curing agents and reactive diluents for epoxy resins.
- The specific chemical structure of phenalkamines provides fast curing and enhances anti-corrosion and surface tolerance. Low-VOC formulations with high performance can be produced.
- In marine and transport coating applications, phenalkamine-cured primers provide good adhesion, fast drying and corrosion resistance. The range of different primers required can be reduced.
- Phenalkamine-cured primers can be applied and overcoated successfully on concrete which has not fully dried out.

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Figure 1: Structure of the cardanol molecule

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\includegraphics[width=0.5\textwidth]{cardanol_molecule}
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Figure 2: Anticorrosive properties (salt spray resistance) of phenalkamine-cured coating compared with polyamide-cured system
Figure 3: Curing speed and pot life of phenalkamine-based primers at different temperatures
Figure 4: Adhesion of coatings on cold rolled steel after 1000 hr salt spray. Right: commercial chromate-free polyamide solid epoxy formulation; Left: phenalkamine based formulation
Figure 5: Coating of “green” (partly cured) high performance concrete, showing increase in adhesion as moisture content of concrete falls.

Figure 6: Schematic representation of blistering test: 1: Concrete is immersed in water, 2: Sides coated after drying for 3-4 hours, 3: Immersion in water for one week, 4: Coating of the surface after re-drying for 3-4 hours, 5: Partial immersion and warming by IR on a cycle of 8hr per 24hr.

Figure 7: Acceptable VOC levels for different markets.
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<thead>
<tr>
<th>Key requirements</th>
<th>Marine</th>
<th>Transportation</th>
<th>Flooring</th>
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<tr>
<td>Surface tolerance</td>
<td>ST2 surface preparation standard</td>
<td>Adhesion to different substrates</td>
<td>Humid substrates</td>
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<td></td>
<td>Universal primer</td>
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<td>Green concrete</td>
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<tr>
<td>Fast curing</td>
<td>One to two coats a day - All season</td>
<td>Lower oven temperatures or faster overcoating</td>
<td>Walkable as quickly as possible</td>
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<tr>
<td>Low VOC</td>
<td>Moving towards high solids</td>
<td>250 g/l</td>
<td>100% solids</td>
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