EPOXY LININGS – SOLVENT-FREE BUT NOT PROBLEM-FREE

Mark B. Dromgool, Managing Director
KTA-Tator Australia Pty Ltd, Melbourne, Australia

Abstract: Solvent-free epoxy coatings have been widely specified and used over recent years in Australia as linings for a variety of immersion service exposures, specifically for potable water storage and tank linings for some petroleum products. However, they have not always delivered the durability or performance hoped for. There have been disappointments and some failures which could have been prevented if a wider understanding existed about the nuances of specifying and applying solvent-free epoxy materials. This paper will outline some of the less-understood aspects of solvent-free epoxies that can result in poor or even disastrous performance once these linings are put into service.

Introduction

Solvent-free epoxy tank linings are a brilliant idea. They are usually a one-coat lining system; they can be applied at high film builds; there is no risk of solvent entrapment; some will tolerate early immersion; they can save a great deal of time and labour; and they combine the generally excellent adhesion of epoxies to prepared steel substrates with a hard tile-like finish. Another major feature is that they have minimal OH&S (occupational, health and safety) issues, i.e., there are no worker exposure or solvent LEL (lower explosive limit) concerns as they do not release any solvent in changing from a liquid to a solid; and they are seen as being environmentally friendly. Other logistic and quality benefits are that they require the shipping, handling and mixing of much smaller volumes of paint on large projects; and they are easy to inspect as they can be made in light colours which aids quality control during application and inspection whilst in service as compared to black coal tar epoxies or other dark-coloured materials.

All of these positive features sound great, and clearly, that was the brilliant idea. What then, are the down sides? There are drawbacks, but too often these appear to be overlooked because they weren't part of the brilliant idea. One of the largest negatives can be the relative lack of tolerance that many solvent-free epoxy materials have to mixing, handling, application and curing conditions when compared to solvent-containing epoxy coatings.

Mixing and handing many solvent-free epoxies is more difficult due to the higher viscosities of one or both components, and these steps generally involve a lot more complicated equipment such as paint heaters, proportioning pumps, static mixers, etc. The more complicated the equipment, the greater the chance that things will not always go right in the field. If mixing and preparation of the coating prior to spraying is not performed correctly within fairly narrow and sometimes unforgiving boundaries, the applied lining can be physically and/or chemically compromised. Spraying solvent-free epoxies is more difficult and much less tolerance exists to properties such as paint temperature and viscosity, spray pump capacity, lengths and sizes of spray lines, tip sizes, continuity of work, etc.

Climatic and substrate conditions are also critical during certain phases of curing. It appears that certain solvent-free epoxy coatings are susceptible to high relative humidity and/or condensing moisture during a certain window of time after application. This can create intercoat adhesion problems or blistering if the coating system involves multiple applications of solvent-free materials.

If these critical issues are not properly addressed or understood, the coating may look satisfactory but it might not work as well or for a satisfactory length of time.

Another negative is the lower chemical resistance of many solvent-free epoxies. High volume solids technology generally involves the use of low molecular weight resins and reactants. A low molecular weight means more epoxide per weight or length of resin which should mean more reactive cross link sites; but to offset this, solvent-free epoxies contain reactive diluents and monoepoxides and these function as internal plasticisers which can lower the chemical or water resistance of the cured film.

Because of the foregoing less obvious drawbacks, the reasonably good rate of success of a few Australian facility owners with solvent-free epoxy linings has not always translated well to other regions, contractors or owners. This means that giving a solvent-free epoxy material to a coating application contractor who has not had any previous experience with it, can result in poor performance and a lot of frustration.

History

Modern solvent-free epoxies that can be applied by single-feed airless spray equipment could be seen as an ultimate evolution of the early catalysed epoxy materials that were first developed in the late 1930s for the dental industry and were adopted as adhesives and then into the protective coatings field nearly 60 years ago. Amongst many other changes, this evolution involved a sequence of incremental formulation changes to progressively lower the quantity of solvent in the wet coating. As a consequence, the volume solids rose from a level of around 45 – 50% in the early years up to the point where liquid epoxy resins were available which could provide 100% solids coating products, that were still liquid until cured.

100% volume solids epoxies did exist as far back as the late 1950s, but these were mainly patching and casting compounds. Sprayable solvent-free epoxies (using plural component equipment) and quite a range of high solids products existed in the 1970s, but some considerable development has happened since that time. The transition, however, from high solids epoxies, at say 85 – 90%, up to 100% solids (or theoretically solvent-free) has not been a small technical challenge. Modern solvent-free epoxy materials are much advanced from their earlier counterparts in that they are formulated using different resins, curatives, additives and pigmentation and their application equipment requirements have changed.

In Australia, the first use of solvent-free epoxy materials as tank linings for potable water started in about 1989. A major urban water authority who managed a large quantity of tanks had a number of OH&S (occupational health and safety) incidents – principally burns from hot materials – with their workers and contractors using a hot-applied bitumen lining inside steel water reservoirs. It was also deemed untenable to continue using these materials in confined spaces due to the inevitable vapour and fumes from the heated bitumen.

At the time, there were many other potable water tank lining products that were still in wide use throughout Australia. Besides the hot-applied bitumen, the principal alternatives were a thin coat of either a solution vinyl or an epoxy primer applied over zinc silicate, some pure epoxy systems or the more ubiquitous coal tar epoxy linings. Some authorities still had pipelines and tanks lined with coal tar enamel.

A local coating manufacturer introduced the water authority to a new material that they had obtained from their overseas parent/affiliate. This material was a two-component, amine-cured solvent-free epoxy. After an initial experiment where the solvent-free product was applied by brush and was seen as working very well, the authority decided to widen the scope of the trial and use this coating as the sole lining for most of their steel potable water reservoirs.

Other coating manufacturers soon entered the market with their own solvent-free materials, most sourced from their respective U.S.- or European-based coatings technology partners. Unfortunately, most coating suppliers and almost all coating contractors who became involved with these solvent-free materials, did not fully appreciate the differences that existed between high solids epoxy linings – which most had some reasonable experience with – and the 100% solids products that had become the new rage.

In essence, the facility owner did not know that much about the peculiarities of the new products he was specifying; the coating suppliers were learning as they went and were not able to provide an appropriate level of practical advice to coating contractors; and the applicators themselves had to try and adapt to lining products that proved to be quite difficult to handle and relatively intolerant to slight changes in climatic and substrate conditions, e.g., changes in relative humidity, temperature drop after application, etc., as compared to the more common high solids epoxy linings.

In hindsight, the decision by the water authority to universally adopt the use of solvent-free epoxy linings, was more on the basis of a perceived environmental benefit; i.e., to reduce solvent emissions to the atmosphere, to minimise possible taint of the water, (assuming that solvent would be the main item causing taint), to avoid extractables from the bitumen or the other lining types affecting water quality, and/or to reduce OH&S risks; rather than for any quantifiable benefit as a tank lining that could not be offered by other materials. This means that the water authority chose solvent-free epoxy for their own perceived set of reasons, and this had little if anything to do with how difficult these products might be to apply or what other negative consequences could result.

The water authority's specification required that the contractor apply the solvent-free epoxy in at least two coats, to achieve a final minimum DFT of 500 microns (20 mils). All work was to be closely supervised by an independent inspector representing the owner's interests, and high voltage spark (continuity) testing was mandatory. The use of an epoxy holding primer was optional, but was frequently adopted by contractors as it usually assisted with logistics, i.e., each day's blasting could be primed with a quick-dry coating, thereafter allowing a much larger surface to be coated with the solvent-free epoxy with fewer joins, once all the surface preparation and priming was completed. Most reservoir painting was performed in the winter months (July and August) as water demands were typically lower through this period.

All too often during these early tank painting contracts, many of the people involved had very little prior experience with solvent-free epoxy materials. There was no shortage of history with more conventional epoxy linings, and few people realised or were told that these new materials were subtly but significantly different. Typically, the coating supplier's technical support person was the local sales representative who was still quite low on the learning curve with these products; the inspector had inspected epoxy linings before but not the new solvent-free types; and the coating contractor's staff had painted tanks with all types of epoxies in the past, and had generally coped quite well. Whilst confidence levels were probably fairly high; there was more than enough inexperience and ignorance to go around. In truth, no one knew what they didn't know.

Not aiding this situation, was the scarcity of good practical information from the coating manufacturers. Probably one of the reasons for this is that many of the manufacturers simply did not know what it took to apply these products under field conditions. Quite a number of product data sheets from the period had no guidance on how to mix and prepare the coating for spraying; and most quoted overseas spray equipment setups that were a straight copy of the information provided by their overseas technology partners and was commonly not available locally or had no direct equivalent. Similarly, information on suitable climatic and substrate conditions before, during and after the coating was to be applied was generally absent or worthless; and dehumidification (DH) equipment or climate control was typically not mentioned. Consequently, the manufacturer's sales staff, the inspector and the coating contractors were often left to their own devices.

Problems

Even though the water authority that first used these materials (and has continued to use them almost exclusively) is essentially happy with the performance and durability of the solvent-free epoxy-lined reservoirs, these linings have actually been far from problem-free. The list of problems that have appeared over the years includes areas of soft coating; delamination between coating layers; blistering from the substrate or between coating layers; the formation of an exudate or sweat; crocodiling of the film's outer surface; poor performance along stripe-coated areas; poor film flow or formation resulting in pinholes or other defects; and the appearance of a "chalky" film.

Other disadvantages of solvent-free epoxies as compared to their solvent-based counterparts are shorter pot lives during application; inferior wetting of the substrate; lower bond or adhesion strengths; lower chemical resistance; a less uniform film structure; higher internal stress levels; higher risk of delamination if multi-coat applications are required; and less effective maintenance characteristics. A potentially lower chemical resistance is very important, because high quality (e.g., potable) water, is one of the most difficult cargoes to hold in a mild steel tank – it is more damaging to an organic film than seawater or even many chemical products.

A Case History Example

After only three years of service in a potable water reservoir, large blisters were noted in parts of the epoxy lining on the tank shell. The blisters were water-filled and originated between the two coats of solvent-free epoxy. Additionally, large areas of the second coat of solvent-free epoxy had disbonded and the adhesion between these coating layers was variable, generally between fair to very poor. The first coat of solvent-free epoxy was securely bonded to the thin-film epoxy primer and no corrosion of the steel substrate had occurred. The visible problems were principally confined to the immersed surfaces below the normal upper water level. The tank was about 44 metres diameter by 12 metres high (144 feet by 40 feet) and consisted of a steel shell and roof structure fitted to a concrete floor.

When the pattern of disbonding and blistering was studied, the extent and type of problems seemed to be strongly related to the vertical bands of the coating on the inner tank shell that corresponded with the repetitive sequence of applying the first coat of solvent-free epoxy from a scissor lift platform. Where a vertical band with very bad blistering and adhesion was found, ones of lesser intensity were usually alongside, improving somewhat with successive bands, and then the pattern repeated itself.

For example, working clockwise around the tank, the first vertical band between 12 and 1 o'clock was quite good, between 1 and 2 had minor problems, between 2 and 3 was worse and from 3 to 4 o'clock was seriously affected with blisters and delamination. The band between 4 and 5 o'clock was good, between 5 and 6 had minor problems, and so on. The field records indicated that both coating layers of solvent-free epoxy had taken about three days to complete right around the tank, and the vertical bands which were in the worse condition, were usually the last areas coated in a work shift, typically ending in the late afternoon. Adjacent vertical bands in better condition were sprayed earlier on the same day. The reservoir was located at the top of a hill and as was typical, the relining work was carried out over the winter months, July and August.

Underneath the disbonding second coat of solvent-free epoxy, could be seen vertical lines of dots or tear-shaped streaks. The finger pointing between the owner, the coating supplier and the contractor included accusations of painting over water, given the quite unique pattern of dots. The contractor insisted that the tank was always dry when they applied the coating materials, although after some searching of the records it was found that the tank was sometimes wet with condensation first thing in the morning due to an overnight drop in temperature and consequential rise in relative humidity. Predictably, the owner's inspector and the contractor's QA system did not allow paint application to start on the following day until conditions improved and the surface was dry and warm, which was typically by late morning. The contractor was very insistent that he had applied the coating fully in accordance with the owner's specification and the manufacturer's written product data sheet.

The facility owner's specification contained typical details with respect to application conditions, humidity and restrictions of climatic and substrate temperatures, however, it was far from comprehensive. The specification contained the following instructions beyond the requirements to comply with the manufacturer's product data sheet and written recommendations:

> *"... no coating application shall be carried out if the temperature is likely to drop below the minimum application temperature or before the previous coating has cured. Epoxy paints shall not be applied with ambient temperatures below 10°C, ... or when the temperature of the steel surface ... is less than 3°C above the dewpoint, or at a relative humidity of greater than 80%."*
>
> *"The (blast holding) primer should not be allowed to become wet with ponded water, etc."*

Ironically, the specification included the above comment that the epoxy primer was not allowed to be wetted, yet it was silent with respect to the same restriction for the subsequent solvent-free epoxy layers. Specifically noteworthy was the absence in the specification of instructions relating to climatic or substrate conditions <u>after</u> coating application and during the curing phase, and there was no requirement or suggestion to use DH equipment.

The manufacturer's product data sheet that was in force during the contract period contained <u>no details at all</u> of climatic or substrate conditions that should exist during or after application.

The coating supplier insisted emphatically that there was no potential for their solvent-free epoxy to suffer from any exudate problems, their reasons being that it was cycloaliphatic amine-cured, and ..."these materials don't do this". The MSDS for the solvent-free epoxy curing agent noted the presence of an organic amine, listed as Isophorone Diamine.

However, the pattern of the failure was revealing, and the subsequent laboratory analysis using IR (infrared) spectroscopy and ATR (attenuated total reflectance) IR was convincing. The laboratory results showed the presence of an amine or an amine salt material and a hydrocarbon-based exudate between the two solvent-free epoxy coating layers. These materials were found in the blister liquid and between the two high build coating layers both above and below the waterline.

What everybody ignored and failed to appreciate, was that the climatic and substrate conditions <u>after</u> paint application are as vitally important as those before and during. What apparently happened after each day of spraying the first coat of epoxy high build, was that freshly applied coating system was subject to condensation with water from the cooling night-time air, within hours of being applied. The last vertical band of the day's work was clearly the most seriously affected with bands that were sprayed earlier in the day being less so. With the coating still being "green" in these areas, i.e., whilst it was still in the process of crosslinking and drying, its outer surface was literally subject to immersion conditions with very pure condensed water. The water droplets on the fresh coating reacted with some of the amine-containing ingredients in the film, and, due to the water solubility of the amine, these materials were pulled from the film by the condensation.

Some amine compounds have good water solubility and can be drawn into condensed moisture on the surface of a partly cured epoxy coating film. The next process involves a chemical reaction between dissolved CO_2 (carbon dioxide) in the water and the amine in the epoxy. CO_2 is much more soluble in water than is O_2 (oxygen), so even though there is nearly 21% O_2 in the atmosphere and only a very small percent of CO_2, there is a good chance that there can be enough CO_2 dissolved in the water. This forms carbonic acid which chemically reacts with the amine, neutralising it and forming a class of compounds called carbamates. This is the archetypal amine blush or amine sweat. The presence of moisture provides the opportunity to extract the amine; the dissolved CO_2 allows it to be converted to a carbamate – without water or carbonic acid this does not happen. Carbamates are oily or greasy and do not react with epoxy. The presence of a carbamate does not necessarily hurt the performance of the first coat of epoxy, from which it was formed, i.e., the loss of a small quantity of amine is insignificant. The primary concern is for disbonding of a subsequent coat layer due to the presence of the greasy film.

In some instances the condensation became so heavy that drops started to run down the vertical walls, enlarging in volume as they went. These became the vertical lines of dots or streaks that were visible after the second coat of solvent-free epoxy had delaminated. Whilst water is good at solubilising the amine, carbamates are much less soluble in water. The most effective way to remove carbamates from the surface of a curing epoxy is to dissolve them in either an alcohol or a ketone solvent, however, no one knew that they were present. Certainly, neither the specification or the product data sheet made any mention or gave any warning of the conditions that could cause these exudate materials to develop. Even the coating supplier, who was the one party who could or should have known that an exudate of amine leading to a carbamate was possible, absolutely believed that the coating product was immune to this effect. If the manufacturer doesn't know or doesn't tell, who else is likely to?

If in the unlikely event there was not enough CO_2 present in the condensing moisture – and given a very large collective surface area of the small water droplets, this is doubtful – then the amine that did not form into a carbamate film, would essentially remain as amine. It is quite probable that the amine would be dissolved into the film of condensed water, but it would not be removed from the surface unless the water dripped off under the influence of gravity. It is expected that any dissolved amine would be redeposited onto the outer surface of the first coat of solvent-free epoxy when the water droplets evaporated.

The carbamate material would be also be present, but it would be beneath the film of condensation until the water evaporated in the warmth of the next morning's weather. It would essentially remain there unless it was exposed to a material in which it was soluble, i.e., either an alcohol or a ketone solvent, which never appeared because the next coating layer was solvent-free. Even though the surface probably appeared to be satisfactory when it was overcoated, it still had a thin film of exudate present.

Even if the inspector or the coating supplier had taken the opportunity to look at the coating, there is a very good chance that the presence of an exudate would have been missed, primarily because it was only every third or fourth vertical band inside the tank wall that was seriously affected. Due to the pot life of the coating and the time to reach a surface dry condition where wetting the surface with condensation would not have a negative influence, many of the vertical bands of coating would probably have been quite alright.

The exudate that remained after the water evaporated would be mostly carbamate. If a new coating layer was applied, this material has no ability to react with or be absorbed by the fresh layer of wet epoxy – it will remain sandwiched between the coating layers as a greasy film. It is worth stressing that the solvent-free epoxy does not contain any solvent, and particularly, it does not contain any alcohol or ketones, which some solvent-based epoxies do have. Therefore, the carbamate will persist. If there is any unreacted amines present on the surface, these will likely react with epoxide groups in the new coating layer, this becoming part of the regular coat-to-coat bonding mechanism of epoxies.

The laboratory analysis showed that there was a "an amine or amine salt" present in the blister liquid and also on the underside of the outer coating layer of solvent-free epoxy. There was also an organic oily material that the analyst simply indicated was "aliphatic carbon-hydrogen," in nature without being specific as to what this was. If a basic (alkaline) material is reacted with an acid and neutralised, the product is often described as a "salt" or sometimes (depending on the reactants) as a "soap." The IR spectras detected the reaction product from the basic amine and the carbonic acid and described this as an amine salt. In fact, this is the carbamate. It is also noteworthy that the hydrocarbon is also a by-product of the same reaction. As the amine (NH_2) contains nitrogen and hydrogen, and the carbonic acid logically contains carbon; one reaction product is a hydrocarbon, which would explain the oily film.

Why had the coating film responded the way that it did after it was immersed? In essence, the outcome was totally predictable. Even though the cured system of an epoxy primer and two coats of solvent-free epoxy had been tested by a variety of means after it was cured – destructive adhesion testing excepted – the presence of a very thin film of a greasy carbamate between the two high build layers would be very hard to detect. Once the potable water was introduced into the tank, water vapour permeation through the lining would have started. This is a totally expected phenomena and is typical of a semi-permeable membrane when exposed to an aqueous cargo.

As the water vapour reached the carbamate layer it will have found an interfacial zone where it could start to accumulate, simply because the adhesion was lower along the plane where the carbamate was present, and therefore, a convenient cleavage zone existed. The accumulation of molecular water and the subsequent blistering was not due to soluble material per se between the coating layers – because carbamates have very low solubility – so the water transmission was not osmotic but simply regular permeation.

It is important to stress that the particular solvent-free epoxy coating formulation that was used on this tank is not defective. It is just that the coating contains certain amines that are absolutely vulnerable to the well recognised problem of amine blush. The curing coating is only susceptible to specific conditions for a certain length of time after application, and in this instance, the problem was mostly limited to the last vertical band or so that was applied during a daytime work shift. Coatings that are applied late in a day are often a concern from a solvent retention point of view – this is a very different problem.

Who should bear most of the responsibility of the foregoing case history? Of all the parties involved; the facility owner, the coating manufacturer, the inspector and the contractor; who should have had the most knowledge about how these new coating products should be handled and applied, and who should have made it their business to be the disseminators of that knowledge? It is worthwhile going through some of the history of the project and relating product data sheets, specifications and other written information to a timeline to see if a pattern and an answer emerges.

The tank was prepared and painted in July 1993. The manufacturer's product data sheet that was current at that time was dated May 1992. This data sheet contained absolutely no guidance information at all regarding climatic and substrate conditions.

When the lining problem was discovered, it was three years later, i.e., in August 1996. There had been two updated versions of the product data sheet over the intervening period, the first dated October 1993 and the second one dated April 1995. These two latter data sheets were almost identical to each other, the main difference being an extension to an overcoating table if the lining had been exposed to direct sunlight. With respect to recommendations or restrictions for climatic and substrate conditions, both of these versions were equally silent. There was more information regarding the heating of the paint through inline heaters or heated hoses, but essentially, there was no more application advice than was contained in the May 1992 version. There was an additional system information sheet that was referenced on the two latter data sheets, but this similarly had no guidance information on climatic or substrate conditions. Even a separate section in the coating data sheet manual on relative humidity and substrate temperature, offered no extra advice. This was extremely general and referred mainly to climatic conditions whilst the coating or lining was being applied, rather than afterwards. The only oblique reference was the following:

> *"In general reduction in temperature leads to a risk of condensation. For instance steel cooled down during the night will often show condensation and this will not evaporate until the steel is heated up again by sunlight or other means."*

This does not warn against the possible effects of water condensing on the coating after it has been applied, and this information sheet was dated February 1994, at least 20 months after the original application.

During the finger pointing after the tank was first emptied and inspected, the coating manufacturer went into print to both the contractor and the tank owner, and:

- Accused the contractor of painting over water, stating that the existence of water in the blisters and the vertical lines of tear-shaped drops indicated that water was present when the second coat of solvent-free epoxy was applied;
- Presented and compared weather bureau information from an outdoor monitoring station several kilometres away from the site, to the contractor's field records from inside the roofed tank and claimed inconsistencies;
- Advised that their tests of the blister liquid showed the presence of a solvent, and they estimated it to be present at a level of 20% (implying that the contractor had added solvent against specification and data sheet instructions);
- Later amended their accusation that the contractor had added solvent and admitted that the organic components in the blister liquid were actually from the curing agent of the epoxy, which leached out when in contact with water condensation (which was known to have been present in the early mornings on some days);
- Concluded that, even though substrate temperatures would have risen to well above the dewpoint later in the day, that "moisture would still have been present and it is the presence of this moisture that is the likely cause of the blistering and poor intercoat adhesion";
- Introduced a new set of climatic guidelines (not previously published) that required that the relative humidity is to be below 50% at application temperatures between 5 and 10°C. Note that the temperature at the time of application was always above 10°C, as per the specification;
- Implied that the contractor had not conformed with the new application guidelines for climatics, even though these were first issued three years after the coating system was applied;
- Advised that their solvent-free epoxy "is not designed for underwater curing or curing with a wet surface." This advice was first provided nearly six weeks after the blistering problem was first discovered; and
- Confirmed again, in writing, quoting their overseas technology source, that their solvent-free epoxy is not susceptible to amine bloom, and neither was this phenomena observed whilst their National Technical Manager was on site and performed a personal inspection.

The facility owner's specification did have some omissions and shortcomings, specifically related to the climatic and substrate conditions that should have existed after the coating system had been applied, not just prior to and during. It also failed to call for dehumidification or any other forms of climate control. However, it is quite likely that some of the key details in the owner's specification were actually led or provided by one or more of the suppliers of a short list of approved solvent-free epoxy products that were contained in an appendix to the specification. If the manufacturer of the product used on this tank, who had been securing the largest share of the tank lining supply over the previous few seasons, had not taken the opportunity to advise the owner of measures that the specification should contain that would ensure a higher quality product and lower both of their risk of problems developing, then this could be seen to be an act of omission.

It is also worth questioning where the coatings inspector and the contractor would turn to obtain relevant and reliable information on new coating products so they can do their work professionally and accurately. It is easy to assume that having experience with other high solids epoxy tank linings would suffice for both of these parties, but the new solvent-free epoxy materials are very much different to many of the old products, so equipment, practices, assumptions and understandings are not often satisfactory.

Clearly, the manufacturer of any new coating product should provide comprehensive information that will reliably aid coatings inspectors and contractors that are reasonably experienced, to properly prepare and satisfactorily apply high performance coating or lining products. In the example of this case history, it seems that the coating manufacturer did not adequately do this important task.

There is an ironic twist in this case which involved the owner dissenting with one of the key recommendations of the solvent-free epoxy manufacturers. The owner wished to have well-applied and defect-free linings for his water tanks. To ensure or encourage this, the owner specified that the contractor was to apply the high build system (excluding the primer) in at least two coats, the theory being that there would be less possibility of concurrent pinholes if the system was applied in more than one application. High voltage spark (continuity) testing of all surfaces was also required. When the program of using solvent-free epoxy linings was initiated, a number of potential coating suppliers advised the owner that their products were normally used as a single-coat system. Presumably, this was on the advice of their offshore technology sources. Not only did this make sense for a technical point of view, (discussed shortly) but it also had a major commercial element.

One of the main selling points for the use of solvent-free epoxy materials as linings is that they would save application time and labour, even if they were slightly more tricky to apply. This had all the predictable benefits of a quicker turn-around for the tank, less cost for scaffolding, a lower labour input, etc. In spite of the arguments by the manufacturers, the owner would not initially relent to a one-coat system. (He did much later when some contractors proved that they could apply a defect-free lining in a single application.) In fact, the owner would not list as an approved product, any solvent-free epoxy material that was required to be applied in one coat. Due to the potential volume of business and so they were not excluded from the approvals list, most manufacturers issued product data sheets that had a recommended coating system that complied with the owner's preference for a two-coat application.

It appears that the technical reasons against the use of two-coat systems was not clearly telegraphed to the owner, to a degree where it could influence the specification for this and other water tanks.

The first question that this raises, is: what exactly was the state of knowledge of the coating manufacturer with respect to the parameters for successfully using their new product at the time that the lining was being applied and when it was later found to have a major problem? At those same times, what knowledge and experience did the sales or field tech service person have versus the formulators or senior technical people? Did the backroom technical people provide good and complete advice and guidance to the sales person to aid him to properly sell and service this new product in the field, i.e., giving accurate, practical guidance to the contractor, the inspector and to the owner?

In short, the tech service function was probably performed by someone who was very low on the learning curve with solvent-free epoxies. Similarly, the inspector most likely didn't have any relevant knowledge of the products he was commissioned to look over, and the coating contractor was learning as he went along because no one had provided him with any advice or guidance, written or otherwise, about how these new materials need to be handled.

What was driving this insane and fated mission? The facility owner wanted to get away from the OH&S issues of using hot-applied bitumen linings; he felt that there were environmental brownie points by using a lining that did not release any solvent; he predicted that water taint from solvent or extractables from the bitumen will go away if he used the new solvent-free epoxy technology that has been promoted to him; and he wanted a defect-free lining so his specification was written to insist on a two-coat system. The supplier had probably rushed a new lining product to market and was either really uncertain or even confused about how it should work. His staff were grossly inexperienced on these new materials and most of their learning was coming at the contractor's and the owner's expense. The contractor was thrown in the deep end with a new product that everyone else was waxing lyrically about, but no one had ever actually learnt its mixing and application parameters and limits. The contractor relied on a grossly incomplete product data sheet and the specification, and they were both silent on key points, because almost all the people involved simply didn't know what they were trying to do and achieve. The problems that appeared in this (and in many other cases) were all unexpected and undesired, however, they were almost totally predictable and inevitable.

Settlement of the Problem

The owner wanted the total coating system fully removed and reapplied, on the basis that he had not received what he believed he had specified or paid for. The coating supplier insisted that his materials were alright and the applicator must have mistreated them. In truth, the coating contractor was about the only entity who undertook his work in accordance with the specification and the product data sheets as they were written.

The owner's specification was somewhat contributory in that it specified that at least two coats of solvent-free epoxy were to be applied. As will be shown shortly, this conflicts with the parameters of these materials. The specification was reasonably descriptive about relative humidity, dewpoint and surface temperature conditions before and during application, but was silent as to conditions beyond the time that the coating was applied, i.e., during its curing phase. For example, there was no requirements to have humidity control or to ensure that the coating be kept free from surface moisture before being recoated or offered for service. Similarly, various versions of the coating manufacturer's product data sheet (as outlined earlier, it had since changed several times in the years since the contract was performed) had conflicting information regarding its preference for a one-coat or a two-coat system and was silent on most key application recommendations. The data sheet version of the original date had no information at all regarding climatic and substrate conditions, dehumidification or any post-application condition control.

In spite of the poor appearance of the lining, with large blisters and sheets of disbonding paint, it was actually deemed to be working very well. The lining was technically fit-for-service, with no compromises, in the two key attributes that a lining inside a potable water tank must possess:

- It must protect the steel tank from corrosion and ensure that it retains its structural integrity; and
- The quality of the water inside the tank must not be contaminated or negatively impacted upon by the lining.

Only when the major contributors to the problem were actually identified, (and this was not the coating contractor as was strongly promoted in the early weeks) was it was ultimately agreed that the lining had not technically failed (if the right definition of failure was used) and it still had many years of useful life ahead of it, purely on the obvious integrity of the primer and the first coat of solvent-free epoxy. If the second coat of epoxy was ignored, as it was paying no effective role in the lining system, it was found that the dry film thickness of the balance of the system, actually closely conformed to the coating manufacturer's normally recommended single-coat system of solvent-free epoxy over a thin-film primer. Additionally, the owner's requirements for a durable and serviceable lining were still being met and it still had residual value, therefore there was no real benefit in fully removing and reapplying it. The coating manufacturer agreed to underwrite the balance of the life expectancy that the owner originally required for the lining as a formal warranty. The coating application contractor had his retention monies returned and the tank was not required to be reblasted. The tank is still in service and is said to be still in excellent condition, some eight or so years later.

Chemistry

Some of the specific problems that solvent-free materials can face, relate to the chemical adjustments that need to be made in order to make the transition from high solids (i.e., containing up to about 90% solids) to a full 100% solids or solvent-free material. In simple terms, because epoxies work by a chemical crosslinking of a resin containing an epoxide ring, (an oxygen atom bonded to two different carbon atoms which are themselves joined by a single bond) and a curing agent or converter which contains amine (NH_2) groups; a sufficient number of amine compounds are needed to ensure that the less-molecularly mobile epoxide group is reacted.

With regular high solids (i.e., solvent-based) epoxies, the coating formulator has a choice of a wide variety of curing agents. In past years, these were commonly aromatic amines and/or polyamides, depending on the properties desired in the cured film. In later times, especially as the demand for higher volume solids materials increased, formulators moved to multi-functional polyamines such as cycloaliphatic amines, and on to polycyclic aliphatic polyamines. This is because to make a true solvent-free coating, all of the liquid ingredients (the resin, the curing agent, any diluents, accelerators, plasticisers, etc.) must not contain any solvent. Because liquid epoxy resins are now quite commonplace, one of the biggest challenges, then, has been to find or develop solvent-free curing agents that still have the desired reactivity.

The choices available for cycloaliphatic amine curatives were essentially limited to two commercial products: cyclohexyl diamine and isophorone diamine. These are single ring structures. To get the polycyclic aliphatics, several companies employed hydrogenation technology to aromatic amines. Explained simply, this involves putting hydrogen in and taking double bonds or aromatics out.

Whilst the cycloaliphatic amines are said to have better molecular mobility and a faster speed of reaction as compared to the more traditional aromatic amines (1), this can be counter productive as there still exists the issue of ensuring that each epoxide group is properly reacted in the drying film, with a functional amine that is in the right place at the right time. This problem arises because of the inevitable increase in viscosity and the thixotropy of a freshly mixed (and applied) solvent-free film.

Having some solvent in the wet coating might be seen by some as being undesirable, (especially in the drive to truthfully call the coating solvent-free), but there are many distinct advantages with having a measure of solvent present, at least during the mixing, induction, application, reaction, drying and curing stages of a coating's transformation from wet to dry. Solvents have much lower surface tensions than resins, and the beneficial wetting action of solvents is not available in a solvent-free film, often to the coating's detriment (1).

This lower surface tension means that a solvent-based coating is more inclined to fully wet out a profiled substrate. An intimately and completely wet out surface profile is essential if a lining is to develop and retain good wet and dry adhesion. It also helps that most solvent-containing products take longer before they gel. Rapid-setting polymer films, especially those that contain larger sized pigment particles, can sometimes not fully wet out deep and angular surface profiles. This can lead to accumulation and cleavage points for molecular water vapour that has permeated the film, which is often a precursor to a drop in wet or dry adhesion strengths. These accumulation points are the locations where corrosion can commence if oxygen is present.

Even a small amount of solvent in a wet coating ensures that at both a macro and at a molecular level, an acceptable level of mobility is retained. The solvent provides lubricity within the wet film – a key feature when encouraging reactive species to get close enough to chemically crosslink before the film freezes. A good analogy is a bowl of freshly cooked pasta, e.g., spaghetti. This is sticky and starchy and does not slide or move freely. In fact, the molecular chains of an epoxy resin are not unlike cooked spaghetti: long, intertwined, sticky and somewhat lacking in ability to move. Add some pasta sauce or some olive oil to the pasta, and the lubricity is provided (1). The sauce or oil is very like solvent. The solvent allows the molecular chains to move and slide. If molecular movement can be retained during the time that the coating is still wet, there is a much better chance that the epoxide groups on the resin and the amine molecules on the curing agent, will get physically close enough to react.

With any reactive organic coating to be used as a chemically-resistant lining, the aim is to encourage more complete crosslinking of the reactive species that are present. This means that with an epoxy material, every epoxide molecule needs access to a reactive amine group and the reaction must run to completion. If both viscosity and thixotropy are high, physical and molecular movement of the reactive species in the film, when the coating is applied to the substrate, may be restricted. If this happens, there will be a greater presence of unreacted, monomer-like zones in the film that are less chemically resistant (1). This is caused by having some unreacted epoxide groups on the resin backbone and amine curing agent molecules not finding partners and becoming frozen in the setting film. This inevitably leads to a higher permeability to oxygen and moisture vapour – both of which are highly undesirable in an immersion-grade lining. With a solvent-based coating, and particularly one that has a nice slow gel time, the chances of a very high order of reaction occurring, are usually very good.

However, in the drive to formulate a solvent-free coating, many of the highly desirable features that the solvent brings to the party are denied. Higher volume solids demands lower molecular weight resins and reactants. This adds to the problem of poor molecular mobility, and the almost inevitable faster gel times that solvent-free materials have, will accentuate the difficulty in ensuring that the two reactive components can get together, or that the substrate can be totally wet out by the coating, to the exclusion of any uncoated zones, before the coating dries and then cures.

At the molecular level, curing is not smooth and uniform, instead it is nucleated and autocatalytic. This means that once it starts, it proceeds more rapidly in those specific areas. It also means that where it starts, it then goes a little faster. This is very much like starting to solving a crossword puzzle, where the presence of a few horizontal words makes it easier to add the vertical cross-links. Whole patches of the puzzle can be done while nearby areas remain untouched. From a practical point of view, there is no such thing as a complete cure. The chemical cure of epoxy resins is a cluster phenomenon and the idea is to make the uncured clusters as small and as uniformly distributed as possible.

So, what do we mean by cure? We speak in terms of adequately cured, satisfactorily cured, and fully cured, and we determine this with comparatively crude tests for hardness and solvent resistance, for example, using pencil hardness and double rub solvent wipe testing. Unfortunately, a completely cured coating with maximum cross-link density for the utmost in barrier protection sounds good but its achievement is a fallacy. Coatings are not perfect barriers to the environment. Water, hydrocarbon solvents, and gases will eventually penetrate a lining and when that happens, the coating needs to have a balance of properties, both physical and chemical, to tolerate the condition.

With epoxy coatings, one possible way to minimise the negative consequences of high thixotropy and poor molecular ability, is for the formulator to add slightly more curing agent than is numerically needed, (i.e., above the stoichiometric ratio) so that there is a better chance that all of the epoxides are reacted, even if this means that some unreacted amine is left over. With the amine groups being molecularly smaller than the polymer containing the epoxide, they are generally perceived to be the more mobile of the pair. However, there is a slight danger in this as unreacted amine compounds that stay locked in a cured film have an affinity for water which can compromise the film when it is used with an aqueous cargo in immersion. By contrast, some unreacted epoxide linkages in the film are usually quite stable in that they are not polar and do not hydrogen bond with water.

Having a slight excess of curing agent in the film, i.e., above what is stoichiometrically required for complete crosslinking with the epoxide, can be tolerated in some situations, but not in many others. If the solvent-free lining application is to be a one-coat system, this can sometimes be of minimal consequence. In practice, some of the excess material (which is principally amine) can be exuded or leached from the surface of the curing film. Once outside the film, if moisture and CO_2 are present, the amine may react to form an amine salt, or more correctly, an amine soap. If so, it will lie on the outer surface as a slightly greasy but principally unreactive layer of carbamate.

The presence of a carbamate film is usually a problem only if it is to be overcoated. This is one of the main reasons why most solvent-free epoxy linings should be specified to be applied as single-coat systems. (It is worth stressing that the generation of an amine sweat or exudate is not limited to solvent-free epoxies – even many high solids materials, especially those designed for early water immersion, can sweat particularly badly – but products based on some cycloaliphatic curing agents are known to be problematic.)

If, however, it is desired or specified that the solvent-free epoxy system is to be applied in two or more coats, then the formation of a carbamate layer on the surface of the first coat, will often be a very undesirable unless it can be satisfactorily removed. The carbamate material is relatively insoluble in water but is quite readily dissolved in either an alcohol or a ketone solvent. Unfortunately, the specified thinning or cleaning solvent for many epoxy products, (and which are likely be available on a jobsite) usually contain quite large amounts of an aromatic such as zylene or toluene, and only small quantities (if at all) of any ketone and/or alcohol. These epoxy solvents will not adequately dissolve the carbamate so it will remain on the outside of the epoxy film. If overcoated without being removed it can act as a very effective bond-breaker between the two coating layers.

When the new lining is being inspected and tested after application, this condition may well not be visible or detectable. However, after the coating is immersed, particularly with an aqueous cargo, serious consequences can occur.

Organic lining films are semi-permeable membranes. Water vapour will start to permeate into and move through the molecular matrix between the atoms and molecules of the resin and around pigment particles of a new epoxy lining within hours of being immersed (2), especially if the density or completeness of chemical crosslinking is low or if the microscopic structure results in an excess of interstitial voids. It is believed that after several days of being wet (even with ponded rainwater) in the case of many epoxy films, the quantity of water intake is already quite high. The time taken to reach an equilibrium with water entering and leaving the film at the same rate, may take longer, i.e., days or weeks, however many variables will affect this.

If there is a plane in the lining system between two separately applied epoxy layers where adhesion is poor due to the presence of an exudate, water will start to accumulate at this interfacial zone. This is not an osmotic influence in this case because the carbamate is not particularly water-soluble so it is not a strong osmotic agent, rather, it is simply the result of regular moisture vapour permeation. In many cases, this will result in the formation of either water-filled blisters or even widespread detachment of the second coating layer if the hydraulic pressure of the accumulating water is greater than the adhesion strength between the coating layers.

The potential for an exudate to develop on solvent-free epoxies is aggravated by a number of conditions. The most pronounced influence is the substrate and climatic conditions during and after the coating system is applied. This includes the substrate temperature, the air temperature, the relative humidity, dewpoint and airflow. Providing DH prior to, during and after application so as to control the dew point, prevent condensation for the narrow window of time when the solvent-free epoxy is at risk, and the problem is essentially solved.

Mixing and Application

Another major influence is the preparation, mixing, induction time, heating and spraying of the coating, and with respect, this is the area where many coating manufacturers seemed to let down their applicator clients for quite some time in the early years by not being able to direct and advise on these crucial aspects. As a consequence, many contractors had to learn at their own expense, often by redoing work or having to suffer other contractual penalties when information or instructions (from specification and / or product data sheets) were often incomplete or wrong.

Mixing and preparing the coating before application is very important and is often not given the consideration that it deserves. The individual components of most solvent-free epoxy materials are extremely viscous. There is also potential for settling out of some pigment components after manufacture, either in storage or during transport. Even in the smaller kit sizes that these products are often supplied in (due to limits of weight nominated in OH&S regulations for manual handling), mixing these components to a state of acceptable homogeneity (both individually and once combined) is a real challenge. These materials are in effect, liquid solids, and there is minimal lubricity because there is no solvent.

Preferably, the individual components should be premixed thoroughly before they are blended and then further mixed. It helps to have the components at a warm enough temperature before mixing, and if this is not achieved, then many negative consequences can arise. The ideal paint liquid temperature is 20 – 25°C (68 – 77°F), and although this often means that the pot life is shorter, the lowering of the viscosity usually means that the mixing is more efficient and quicker, and the energy that the reactive species have, is higher.

Getting the paint components to the ideal pre-mixing temperature can be difficult, especially in the winter. If paint is stored directly on a concrete floor, it will soon adopt the temperature of the floor. This can often be well below 10°C (50°F). A hot water immersion bath is one way of elevating the paint's temperature prior to mixing. Another way is to have a dedicated storage shed that is heated, or even a compressor room or boiler house that is thoroughly warm. In this case, the paint needs to be in the warm storage at least overnight, (say 12 hours minimum) prior to use. Putting the paint on a pallet with a canvas tent from behind the aftercooler of a portable compressor, or leaving the drums in the sun is not effective as the heat distribution and transfer is extremely variable and inefficient, even within different parts of the same drum. Having paint at too cold a temperature prior to mixing, induces the biggest variability in the cured coating and causes the largest problems with solvent-free epoxies.

Many application and performance issues can be minimised if a continuous process of mixing, heating and spraying the coating is followed, such as would occur during the airless application of multiple drums of coating to large flat steel surfaces. In this case, the time between physically mixing the product and its application to the substrate, would usually be very consistent, especially if the work scope existed over a number of hours.

For example, with good access a spray painter can probably apply 20 litres (5 gallons) of a well mixed solvent-free epoxy in 10 or so minutes. If a continuous process of mixing and spraying is established – which is the only way that these products can be handled – each drum of paint would probably be in a mixed liquid state before being deposited on the surface, for between, say, 15 and 25 minutes. If spraying is not interrupted, then this time would be relatively consistent right through the full window of application. (We will later show that this consistency in time, evaporates when spot repair painting work or stripe coating is performed using hand application methods.)

One point that must be stressed in relation to the time that the catalysed coating remains mixed, is that an airless spray pump will often only pull paint from the centre of the feed container, irrespective of whether it is a siphon feed or a bottom-outlet hopper. If sequential drums of fresh paint are added as the liquid level drops in this container, some of the older mixes of paint will remain against the outer walls. These will have a totally different induction time than the fresh material and it is important that a regular sequence of scraping this older material down and remixing the product is performed. If not, parts of the coating in this container will get beyond its pot life and will gel and/or cure. This leads to poor film chemistry and risks tip blockages.

The second most important aspect of preparing the solvent-free epoxy coating for spraying involves getting the mixed paint up to an appropriate temperature to apply. This temperature is higher than what is ideal for storage prior to mixing. This involves the heating of the mixed product as it passes through an inline heater after the spray pump and before the fluid tip. Elevating the temperature of the mixed paint to approximately 35 – 40°C (95 – 104°F) lowers its viscosity and significantly increases molecular mobility. Both of these are very positive features, but consistency and balance is very important.

A lower viscosity coating will atomise easier and better through the spray tip. It will also flow out better to form a continuous film and will wet out the profiled substrate in a superior manner. Elevating the temperature lowers the viscosity, increases the speed of the epoxy:amine reaction as well as increasing the energy that individual chemical groups have to allow them to find a reactive partner. It also shortens the pot life, which is why it is vital to have consistency in this temperature. At 40°C (104°F), the pot life of many commercial solvent-free epoxies can be less than 10 minutes. It is important to understand that an inline heater will achieve the required temperature of the pumped coating within the accepted tolerance, only if the rate of flow of the coating through the spray lines and its incoming temperature are constant. However, depending on the physical arrangement of the inline heater, it may be possible to recycle the paint until the right temperature is reached.

The rate of flow of the coating through the heater needs to be consistent, and the only way to achieve this is to be spraying continuously. It is not acceptable to be working on multiple levels of a scaffold, for instance, and have the spray painter put down the gun whilst he climbs from one scaffold level to the next before he starts again. This stops the flow of paint and risks overheating the coating in the heater. The best approach is to have another spray painter already positioned on the next level, the spray gun is passed to him and he starts spraying without a break. Spray tip blockages are a large problem unless quick-reverse tips are used which allow the blockage to be cleared and spraying to continue within seconds.

Even with the above continuous mixing, heating and spraying sequence, it is common that the spray lines would need to be flushed out with solvent after a number of litres have been sprayed. During a day's spraying, the lines may need to be flushed twice or maybe even more often. Sometimes, after 100 – 120 litres (say 25 – 30 gallons), the lines need to be flushed with solvent. If this is not done religiously, some of the older mixes of paint material that have remained against the outside of the container from where the airless pump is feeding, or have been in contact with the inner walls of the spray lines, will gel and start to cure. This will slow down the rate of flow, change the transfer rate of heat to the flowing material and will raise the incidence of spray tip blockages. It could even cost the applicator a set of spray lines, the fluid section of the airless spray pump or the inline heater; if the hot epoxy cures in the line.

The other variable in the heating and spraying process, (besides the flow rate) is the incoming temperature of the paint as described earlier. The more constant that this is, the more consistent is the heat pick-up from the inline heater. This helps explain why unevenly heated paint materials that have not been stored in a controlled and heated storage, give a variably cured product.

The last item to discuss on the topic of application, is the spray tip. In spite of the advice of many manufacturers with respect to tip sizes, practice has shown that a smaller tip is usually much better. Many product data sheets recommend tip sizes between 0.53 – 0.79mm (0.021 – 0.031 inches). Experienced solvent-free epoxy applicators have learnt that smaller tip sizes, typically 0.53mm (0.021 inches) or less are much better at atomising the coating, but these will only work if the paint is close to 40°C (104°F) at the tip. Some contractors report that they start spraying with an 0.63mm (0.025 inch) tip and then switch to a smaller size as the inline heater and paint temperature rises and stabilises. It seems that forcing the hot coating through a small tip induces a better break-up, more movement, agitation and shear at molecular level, and better wetting of the substrate. It also appears that the combination of the right spray temperature and a small tip size, gives a film that has less voids and a more closed film, resulting in less defects that would be detected with a continuity tester (high voltage spark tester) after curing.

Conversely, if the paint temperature is too low and the tip size too large, the coating will appear to spray satisfactorily, but will not flow out as well. This often results in an application that does not form a closed film when wet, even at quite a high wet film thickness. This invariably results in many spark-through zones when continuity testing is performed.

In our opinion, the key issues of paint storage temperature, spraying temperatures and pressures, tip sizes and the number and thicknesses of coats in the solvent-free epoxy system; were aspects that were not very well understood by some coating manufacturers in the early days of marketing these products, and still too commonly, many field tech service staff do not know which combinations of equipment and material preparation are required for satisfactory application and performance.

Stripe Coating

The foregoing describes what can and should happen when continuously spray applying solvent-free epoxy materials. A very different set of conditions occur when spot repair or stripe coating is attempted.

Unlike most solvent-based epoxies, virtually all solvent-free materials have a very short pot life. This is typically between 30 to 60 minutes after mixing at about 25°C (77°F). If a reasonable pot life is to be achieved to allow for effective spot painting or stripe coating, the coating cannot afford to be too elevated in temperature. The consequence of this is that the high in-can viscosity prevails which is a serious impediment to adequate mixing. Adding solvent to lower the viscosity and to aid mixing is forbidden as these products have a very low tolerance to field-added thinners as this changes the chemical nature of the material, risks solvent entrapment even more than with a conventional solvent-based epoxy lining, and alters the rate and degree of cure.

The applicator therefore has a quandary: does he leave the materials as cold as possible to get enough pot life, risk not having complete mixing and struggle with applying a viscous material; or does he heat the components, thereby lowering the viscosity which aids mixing and makes application easier, but seriously shortens the pot life? There is no best answer but the former procedure normally prevails in spite of its negatives.

The best procedure if stripe coating is required, is to use a compatible solvent-based epoxy as the stripe coat. In spite of arguments to the contrary, this does not jeopardise the integrity of a lining for potable water service as there are many solvent-based epoxy coating products that are fully potable water-approved.

A second issue is effective proportioning of the components when a mix is to be made that is not a full kit. Solvent-free epoxies are typically packaged in 10 litre or 20 litre kits. To mix up one to two litres for touch-up, some skill is needed to ensure that the correct ratio is proportioned from each can. With extremely high viscosities present, this is almost impossible and experience shows that this is wrong much more often than it is right. Wrong mix ratios result in solutions which are stoichiometrically incorrect by a significant margin which causes an increase in unreacted components and compromised chemical and physical properties.

The consistency in time between mixing and application now gets stretched in both directions. As soon as touch-up material is mixed, the applicator must start doing spot repairs, and all too commonly, the balance of the product goes off in the paint can by reaching its pot life before it is all consumed. This means that the time of application after mixing will range from about 5 minutes to 45 – 60 minutes, or even less on a hot day.

A point often forgotten is that pot life depends on ambient temperature but it also depends on material temperature and that means exotherm needs to be taken into consideration. Mix the same epoxy material in a four litre (one gallon) kit and also in a 20 litre (five gallon) bucket and compare the pot life. The key is the paint volume to surface area ratio. Small volumes have a longer pot life because they have a much better volume to surface area ratio.

The significant effect of this long variation in time after mixing is the effective length of the induction time. Whilst still in the can, the exothermic heat of reaction will slowly lower the viscosity (up to a point) which aids molecular mobility and the rate of chemical crosslinking. As soon as the coating is applied, it will adopt the temperature of the substrate and will start to gel, but the molecular mobility will be retarded by the lack of fluidity and a much smaller mass of uncured coating.

If a single mix of touch-up material is applied over a time range of (say) 5 minutes to 45 minutes after mixing, there will be a discernable difference in the chemical nature of the cured film with it being pre-optimum before some mid point, and post-optimum after. This chemical difference will affect properties such as the rate and completeness of cure, the adhesion, permeability, the potential to generate an exudate, and most definitely, the chemical resistance of the resulting film. This condition is visible to an experienced eye as a progressive change in colour of spot repair areas or stripe coats from a single mix of coating.

Also common is the delamination of a high build spray-applied solvent-free epoxy coating off the stripe-coated areas inside a tank, purely because the earlier stripe coating was brush-applied by hand using batch mixes of material. Oftentimes this has a different constitution depending on how long the material has been mixed and can sometimes be seen to change along the length of one single longitudinal weld inside a large tank.

Stripe coating the edges, welds and corners is an important aspect of successfully lining a storage tank, and if a solvent-free epoxy has a low tolerance to this task because it is difficult to mix, is hard to brush, has poor wetability and varies chemically due to the length of its induction time; then this adds to the overall intolerance and lack of user-friendliness of solvent-free epoxy materials.

Riveted tanks or deeply pitted substrates, (whether concrete or steel) are not the best items to be coated using solvent-free epoxy linings. In both cases, the amount of stripe coating or spot repair that is needed, can negate the other possible benefits of considering solvent-free epoxies. Solvent-containing, high solids epoxies are much better for these types of tanks or surfaces, because they mix better and more thoroughly, have a longer gel time and a lower viscosity, which means that they flow into pits, wet the substrate better and can be applied more successfully along welds and around rivets.

In spite of arguments to the contrary (mainly by the solvent-free epoxy manufacturers) there is minimal evidence of solvent entrapment where localised pits or minor overbuild has occurred where a high solids, solvent-containing epoxy tank lining has been properly applied and correctly ventilated. The solvent that is contained in a high solids epoxy, has a much better chance of being released from the curing film, than if an even smaller amount of solvent happens to be added (against instructions) into a solvent-free material. High solids epoxies are designed to release solvent but 100% volume solids materials are not.

Summary

Tank lining work performed in colder climates throughout the winter months, has a higher risk of problems developing problems if solvent-free epoxy lining materials are used, unless specific and regimented protection methods to control climatic and substrate conditions are enforced, and very detailed mixing, preparation and application procedures are followed.

Solvent-free epoxy coatings are specialised materials, but they are more difficult to handle and are far less tolerant to mixing, application and weather/substrate conditions as tank linings as compared to solvent-containing high solids epoxies. The transition in properties and requirements, especially through the mixing and application stages, is a quantum leap from what is required for (say) a 90% volume solids material, to one that is solvent-free. Few contractors have fully learnt the key parameters of these products, and if the correct sequences and methods are not followed, poor performance will usually result. There are few other coating materials that are so difficult to learn and pick up as an applicator because many of the well-proven and long-known principles of mixing and applying high solids epoxies, do not relate in any way to what is needed for solvent-free products. Also, many manufacturer's representatives, unless they have spent many days on site with their arms deep into the paint trying to solve application problems, have not advanced too far from the "it works fine in the laboratory, why can't you get it to go properly out in the field" retort.

Often the comment that is made by the suppliers is that there are OH&S and environmental benefits with using a material that is 100% solids, but is the lining system actually solvent-free if an epoxy primer is used (as it usually is) that is solvent-based? Also, in Australia (at present) there is no VOC regulations covering solvent emissions from paint materials. Even if there was, does a small amount of solvent being emitted compensate for a solvent-free lining that does not work as well or for as long, and is required to be redone earlier?

In summary, solvent-free epoxy linings:

- Are viscous, thixotropic and have short pot lives;
- Are difficult to mix fully;
- Are highly intolerant of field-added solvent as this compromises the rate and degree of cure and lessens the service life (1);
- Are critical with respect to their temperature prior to mixing;
- Require heating to about 40°C (104°F) through an inline heater or similar prior to being sprayed;
- Require more expensive application equipment with a higher risk that the coating may set in the lines or pumps rendering them unserviceable;
- Should usually be applied as one-coat systems;
- Are much more likely to allow an exudate to be released from the coating;
- Are intolerant to disruptions during spraying;
- Are very sensitive to high relative humidity and/or temperature depression during and after application;
- Generally require dehumidification to ensure that climatic conditions remain acceptable within a very tight range
- Are very intolerant materials to use as stripe coats or for spot repair;
- Are less chemically resistant because of a lower density of crosslinking and the higher chance of having unreacted epoxide or amine species in the cured film;
- Can have a higher permeability due to a lower completeness of crosslinking;
- Require a higher film build, and hence more coating product, to provide equal permeability resistance;
- Have higher internal stress levels;
- Exhibit inferior wetting properties to a profiled substrate;
- Have lower wet and dry adhesion; and
- Have less flow as a wet film due to their viscosity.

By contrast, well formulated solvent-containing high solids epoxy tank linings:

- Are easier to mix and have a longer and more usable pot life;
- Can accept some site-added solvent to help make the coating system adjust for different climatic or substrate conditions and to suit the available application equipment;
- Usually result in more uniform film build and less chances of overbuild;
- Have a slower gel time after application which aids flow into the surface profile and assists release of air from the film;
- Are quite tolerant of a variety of weather, substrate and other application conditions;
- Allow a more controlled cure to develop;
- Multiple coats minimise the chances of concurrent pinholes or defects;
- Are designed with tolerance to being applied as multiple coats without compromise;
- Are less likely to form an exudate from the curing coating;
- Have superior wetting due to the lower surface tension that the solvent brings to the resin binder;
- Apply well as stripe coats without the compromises to their chemistry and integrity due to variations in the effective induction time;
- Can achieve higher crosslink densities and more complete cure due to the lower viscosity, more lubricity and hence better molecular mobility of the reactive species;
- Have lower internal stress levels; and
- Are much more easily handled by coating application contractors with a variety of skill levels.

On the basis of the above, we question the widespread and even blind acceptance of solvent-free epoxy systems for tank linings and similar immersion service, as compared to the tolerance and forgiveness of a range of many excellent solvent-based epoxy linings. Can we afford as an industry, to be experimenting with state-of-the-art materials at the facility owner's expense, when the owner is likely to be the party disadvantaged if the latest technology does not deliver service lives or performance that is any better than what we know works extremely well?

In closing, an appropriate quote from Mike O'Donoghue et al. (1):

"Small mistakes with one-coat systems have the potential for far bigger consequences than small mistakes with multicoat systems."

And another from Mark S. Schilling:

"New and poorly understood plus inexperience equals Ouch."

<u>References:</u>

(1) M. O'Donoghue, R. Garrett, V.J. Datta, E. Swanson and B. Dillingham; "Fast-Cure AHC Epoxy Coatings for Tank and Pipe Applications," Materials Performance, June 2000, NACE International, Houston Texas.
(2) E. Hemmings, Ameron (Australia) Pty Ltd, private communication, July 2004.

Considerable appreciation and credit is given to Mark S. Schilling for his extensive input, advice, editing and reviewing of this technical paper.