Corrosion-proof Maintenance Surfacings

Pulp & Paper Mill Applications

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Introduction

Pulp and Paper Mills represent the most challenging of all industries in the protection of concrete and steel. Application of corrosion-proof maintenance surfacings requires full cooperative team effort on the part of plant personnel, consulting engineers (if retained), suppliers and contractors. Any player on the team not pulling one≈s weight will short circuit the process and reduce the chances for success.

Selection of appropriate corrosion-proof surfacings to protect against a myriad of harsh conditions is difficult. Certain surfacings will protect against specific chemical exposures at ambient temperatures, but may not function particularly well at elevated temperatures. Many surfacings will work at elevated temperatures, but will disintegrate under elevated temperatures in wet conditions. And, the list goes on.

Understanding surfacing behavior is critical to success, and the onus of successful applications is placed upon those involved in specification and design. The specifier must understand not only surfacing behavior, but also must be knowledgeable about the conditions or exposures under which the surfacing must perform. Involvement of plant personnel who understand their particular plant and process conditions must have input in the surfacing selection process.

In any industry or plant, rehabilitation is more difficult than new construction. Demolition and removals must occur prior to construction. Preparation of an existing substrate or creation of a new substrate is required for successful application. Increased demands are placed on the specifier, the plant, and the installer, whether in-house or contractor.

Most resinous chemical resistant surfacings require sufficient time for proper substrate preparation, application of multiple layers and cure times. Installation of even the best of surfacings over a poorly prepared substrate will result in adhesion loss. Corrosive reagents quickly and always intrude Ąpinholes∆ or openings in surfacings, thus the need for multiple layers in a corrosion-proof system. Succeeding layers must be applied over cured layers. Time is needed for cure.

Corrosion-proof surfacings are used to resist attack by certain reagents. Time is required for the resins to cross-link, to Ąharden,∆ to become dense. Hardness and density cause the surfacing to become impervious. If the surfacing is subjected to chemical attack before it cures, final cross-linking will not take place, and the surfacing will not achieve specified resistance to the exposure.

Certain environmental conditions are also necessary for corrosion-proof surfacings to cure properly. Substrates must be clean and dry for the surfacing to bond.

Substrate and ambient temperatures must be maintained at a specified range for the resins to cure. The surfacing system cannot be contaminated with dust, dirt, moisture or chemicals from application to cure. If any of these prerequisites is not achieved, specified performance of a selected system is at risk.

Surfacing requirements make no exception by industry. Whether an application be in a dry storage area in a plating plant or in a bleaching tower in a pulp and paper mill, surfacings require the same conditions in which to bond and cure. The difference is providing a favorable application environment, or dealing with an environment that is not so favorable.

Challenging conditions, as first mentioned, are a way of life in pulp and paper mills. Most substrates, steel or concrete, that require chemical resistant surfacings are wet and saturated. Attack by aggressive acid and caustic exposures is compounded by elevated temperatures.

Rehabilitation under these circumstances is a difficult challenge. Application of corrosion-proof surfacings in maintenance situations in paper mills is generally made even more challenging by the lack of time available to execute the installation properly.

This work is not, by any means, an exhaustive study of corrosion-proof surfacings. Nor is it a lesson on chemical make-up. Rather, this work is a primer on corrosion-proof surfacings that have a place in pulp and paper mills under maintenance conditions.

Those readers who are charged with selection and application of corrosion-proof surfacings must be able to evaluate surfacings and their potential to be applied successfully in particular environments. Often, selection becomes a compromise.

The object of this work is to assist those who have to make those distasteful compromises in order to function in the real world.

CHARACTERISTICS OF SOME RESIN SYSTEMS

Consider all resin systems

The first and last maxim that must be understood, and cannot be overstated, is

There is no single cure-all resin system that will work in all cases.

Every generic resin system has unique characteristics in behavior that will make its selection favorable in some instance. Do not discount any system. Do not favor any one system. Or, at some point a system will be overlooked that could solve a particular problem.

Granted, some resin systems work more often than others in mills. But, in mills especially, conditions and requirements are so varied, that a full arsenal of corrosion-proof surfacings is required.

Vinylester

Vinylester surfacings are known for their excellent resistance to a broad range of chemicals and solvents, and have been used extensively in pulp and paper applications since the 1960's.

Vinylester resins are used as grouts in acid brick, fiberglass-reinforced linings, flake-filled coatings and in spray-applied systems, with or without fiberglass or mica flakes.

Fiberglass or mica reinforcement, either in the form of fabric or flake fillers, reduce permeation by moisture vapor, thus increasing resistance in immersion or wet environments at elevated temperatures.

Silica, aluminum oxide, carbon and other aggregates, sized from 200 to 300 mesh powders to 1/8" stones, are also incorporated into resinous mixtures to create troweled mortars. Vinylesters have a high incidence of curing shrinkage, and fillers help to mitigate this characteristic.

Further, vinylesters are brittle by nature and filler addition helps to prevent these systems from cracking when applied over approximately 10 mils, the practical limit of unreinforced or unfilled vinylester system thicknesses. Linings and mortar systems can be successfully applied in thicknesses up to about 1/4" when reinforced or filled, but even then, the systems must be installed in layers.

Differential movement between substrate and resin system is a problem. The systems have a high coefficient of thermal expansion compared to steel and concrete substrates. Fillers help to alleviate this problem.

Although addition of fillers help to make the vinylester systems less brittle, fillers also have a tendency to make vinylesters less chemical resistant than unfilled systems. But, the resistance reduction is only by degree. More chemical resistant systems that disbond due to differential movement are of no use. More flexible, filled systems that will stay in place certainly have more value.

Few other resin systems can withstand 212ÊF immersed exposure to harsh acids and caustics. Although many systems can withstand dry heat to much more than 212ÊF, including vinylesters, not many other systems can withstand immersion over 180ÊF.

Vinylesters cure relatively quickly compared to many other resins, as long as substrate and ambient temperatures are at least 50ÊF. If temperatures fall below 40ÊF for an extended period of time, the resins may never cure, even after the temperature rises. Application of vinylester systems at temperatures over approximately 120ÊF can cause excessive pinholing, bubbling and cracking.

Adhesion of vinylester systems requires dry substrates. Vinylesters are very Ąmoisture intolerant,Δ and will not bond well to a damp or wet substrate. Further, during application, the substrate and ambient temperatures at the work site should be at least 5ÊF above the dew point.

ĄNovolac-basedΔ vinylester resins are of particular interest to the pulp and paper industry, because of their increased thermal stability and chemical resistance over other types of vinylesters. More reactive than other types of vinylesters, these systems offer a greater range of chemical resistance and thermal stability.

Vinylesters are very high in odor. Application of these surfacings when plant production people are in the project vicinity generally results in safety or personnel problems. Workers must wear respirators and plant personnel should not be allowed in the immediate work area without respirators as well.

Vinylester, as well as all resin systems, are made available in a variety of formulations by corrosion-proof surfacing manufacturers. Data sheets are often produced from information received from Ąraw materials suppliersΔ without actual testing accomplished by the surfacing formulator. On-site testing should be undertaken as often as possible to assure expected results.

Some formulators, like people, are more honest and forthright than others. Many will say and publish information that is very enticing. Because the written word is powerful, many specifiers take written information for granted. When involved in any project, especially a critical project, it is very important to detail conditions and expectations to those manufacturers whose products are intended for use. When pressed, nearly every one will advise an on-site test.

On-site testing provides both the owner and manufacturer with performance information, and helps to protect the specifier from a design disaster.

Epoxy

Epoxy resins were first developed in the 1940's, but really came into prominence during the late 1950's and 1960's as zinc-rich primers were being used with more and more regularity. An alkaline reaction (saponification) between zinc-rich primers and alkyd coatings led to development and use of epoxies over these primers for corrosion control applications.

Excellent adhesive properties of epoxy were discovered to apply both to steel and concrete. Formulations for both substrates have evolved over the years to current use, and research is continuing on a global scale.

Without getting involved in chemical make-ups, most epoxy resins for steel and concrete surfacing applications are of three types: Bisphenol A(cetate), Bisphenol F(ormaldehyde) and Multifunctional Novolac. Considering the resin make up of an epoxy formulation is normally at least half and usually more, system properties such as chemical resistance and heat resistance are greatly affected by resin choice.

These epoxy resins can be combined with various curing agents or hardeners, such as Amides, Aliphatic Amines, Cycloaliphatic Amines, Aralaliphatic and Ethylene Amines. (There are others). Further, various combinations of curing agents can be used with any resin to create a specific system to resist particular exposures, or to create a system with certain desired characteristics.

Bisphenol A Resins are the traditional backbones of epoxies. ĄBis AΔ resins are now general purpose epoxies and were first developed for steel and concrete surfacing uses. High in viscosity compared to Bisphenol F resins, additional diluents and solvents must be added for coating use. The additives, in general, tend to reduce chemical resistance and increase VOC, a problem throughout our industry.

Bisphenol F Resins, when combined with selected hardeners, are significantly more chemical resistant than Bis A systems. Bis F resins have more reactive sites with which to cross-link than do Bis F resins, making the system denser. These resins are widely used for Ąchemical resistantΔ surfacings.

Multifunctional Novolac Resins have the highest potential for chemical resistance than the other resins. Novolacs have the largest number of reactive sites with which to cross-link, making the surfacing denser and more impervious to chemical intrusion. When novolac resins are combined with specific curing agents, the system can withstand high temperatures and exposure to aggressive acids, such as 98% sulfuric.

Novolac systems are higher in viscosity thus require the use of diluents to reduce viscosity. Formulation of these systems requires meticulous attention to detail to achieve specific resistance to chemical exposures and aggressive solvents, while still remaining workable in the field.

Functionality is a measurement of the number of cross-linking or reactive sites in a chain of resin molecules. Higher functionality generally increases hardness and cross-link density, which increases chemical resistance.

Functionality of Bis A Resins is about 2.0; Bis F Resins about 2.3, and Novolac Resins about 3.0 to 3.6. Generally, novolacs with functionalities over 3.0 are not Ąpretty.Δ Gray finishes turn green, reds turn a rusty brown and color uniformity is only uniform in its lack of uniformity. Always ask a manufacturer about color uniformity of their novolacs, because if they promise color uniformity, the functionality is normally relatively low. If the functionality is low, the chemical resistance is likely lower than other novolacs available.

Amide Curing Agents are the most user-friendly of hardeners, having fairly long pot lives and less critical mix ratios. Amides, however, are generally the least chemical resistant hardeners. Although beneficial for use for moisture tolerance and alkali resistance, amides are generally low in heat resistance. They cure slowly compared to other hardeners, which is advantageous for wetting characteristics, but may be disadvantageous in a fast turn-around project.

Amide curing agents are not as hard as other curing agents, thus are more flexible, which may be beneficial in certain applications, especially over steel. Typically, epoxy systems utilizing amide curing agents must be ĄinductedΔ or Ąpre-reactedΔ for a specified time before application, in order to initiate proper cure.

Aliphatic Amine Curing Agents provide hard, tightly cross-linked surfaces, and are often used in the composition of chemical resistant epoxy systems. They offer fast curing properties that are helpful in many situations. Aliphatic amines have some draw backs, however. Some people are allergic to them and become sensitized.

Also, in general, they are moisture sensitive and curing and performance properties can be adversely affected if applied and cured in the presence of moisture.

Another feature that must be taken into consideration with aliphatic amine curing agents is the fact that they develop an Ąamine blush.Δ Particularly if cured in damp or humid environments, a greasy, oily film may rise to the surface. If succeeding coats or layers are applied over this film, Ąfish eyesΔ and/or Ąintercoat delaminationΔ is likely to occur. The blush must first be removed by washing with detergent and water, rinsed and dried

Aralaliphatic Amine Curing Agents have limited chemical resistance, but do not incur amine blushing and allow for low temperature cure. Formulations allow for resinous systems to be applied as low as 35ÊF and still achieve a tight, dense surface.

Ethylene Amine Curing Agents provide excellent cross-link density and outstanding solvent resistance when formulated to be used in combination with appropriate resin systems. Amine blushing is a by-product of this system, and must be considered.

Cycloaliphatic Amine Curing Agents have good chemical resistance and blush resistance. Cycloaliphatics are used widely as curing agent components to chemical resistant systems. Certain formulations (not all) provide moisture insensitivity and high abrasion resistance, as well as excellent thermal resistance.

Epoxies and epoxy systems offer enormous varieties of combinations. That≈s the good news. The bad news is raw epoxies are available to just about anyone who wants to buy them. Our market place is full of Ąepoxy suppliersΔ who have acquired ĄrecipesΔ and turn finished products out the door with data sheets touting unusual performance.

Specifiers, Owners, and Contractors, the design/installation chain, must approach corrosion-proofing as a team, share information, and objectively interview manu-facturer/formulators to determine appropriate systems. Reputable manufacturers will fully participate in this process to verify successful potential for their products≈ use. No reputable manufacturer wants a failure.

Methyl Methacrylate (MMA)

Methyl methacrylates are extremely fast curing, resinous systems primarily used for concrete surfacings. Although not particularly suited for use in wet, high elevated temperature and aggressive chemical exposures, methyl methacrylates offer unique benefits.

MMA≈s can be formulated to cure at sub-zero temperatures, many as low as -10ÊF and some lower. Upper range application limit is about 100ÊF.

Very moisture sensitive, MMA≈s must be applied over very dry substrates, but when properly applied, the bond is very tenacious.

They are high in shrinkage, so to compensate, aggregate loading is a must.

MMA≈s are very good concrete patching materials where speed of cure is important. Some forumulations can be mixed, place, cured and ready for traffic in less than 15 minutes.

They exhibit good physical strengths and wear well under traffic.

Suseptible to degradation from solvents and corrosive acids, MMA≈s are better used in general purpose areas such as traffic aisles and other concrete areas where need for aggressive corrosion resistance is reduced.

Methyl methacrylates also exhibit excellent resistance to ultraviolet light.

Although not toxic, MMA≈s are very high in offensive odor. Application should be limited to areas and time frames when plant personnel will not be present.

Urethane

Urethane enamels are not particularly resistant to aggressive chemical attack, especially at elevated temperatures. Like MMA≈s, they exhibit excellent UV resistance. Urethanes are excellent for exterior use and provide a hard, abrasion resistant film.

Adhesion is marginal when applied directly to a substrate, but bonding characteristics can be greatly enhanced with use of epoxy primers. After epoxy primers are applied, application of urethane must follow within a precise ĄwindowΔ of time to ensure maximum adhesion.

Polyester

Polyesters and vinylesters should be grouped together in discussion, because of their similarities, but for this work, have purposely been separated. In general, vinylesters and polyesters exhibit similar shrinkage qualities and require fillers as previously discussed. Polyesters, too, are very moisture sensitive and will not bond well to a damp substrate.

Polyesters, as well, can withstand elevated temperatures in corrosive environments, however, polyesters do not have the same degree of broad range chemical resistance as vinylesters--though they are not far behind.
Particular formulations of polyester, however, offer better resistance to aggressive oxidizers such as chromic and nitric acids, and should be remembered for those properties.

Further, specific formulations have been Ąre-discovered∆ to be more resistant to Chlorine Dioxide than even novolac-vinylesters, under wet, elevated temperatures. Further discussion of this attribute take place later in this work.

Summary

Other corrosion-proof surfacings are available than those described, however, this work is focused on maintenance. The systems covered are the back bone of corrosion-proof surfacings useful in pulp and paper in maintenance environments. Some good ones may have been omitted, but this work is a start, and only meant to be that.

The same approach and thought process can be used for systems described, as well as those omitted, or not yet invented.

Although chemistry is a fairly exact science, its interpretation is subject to argument and debate, among very educated minds. Selection of corrosion-proof surfacings among choices offered commercially is even more inexact. Authorities in our industry offer definite opinions based on their knowledge and experience, but those views often conflict with each other.

How can we, specifiers, owners and contractors, who know far less than our learned counterparts, determine selection and application of a system that will function under our conditions?

> We take nothing for granted. We read. We study. We research. We discuss. We test under actual conditions. We assemble expert information

with our information. Then, we make joint judgements.

We need to do these things, because many times, in maintenance conditions in a pulp and paper mill, we will have to compromise using the best system in favor of a lesser system. Prerequisites required for proper application and cure of resins, as we have seen, are not necessarily available on the occasions we need to make repairs. So we need to make compromises. Let them be educated compromises.

The Maintenance Challenge

Determination of exposure is critical to surfacing selection. All facets of the exposure should be explored: exact chemical make-up, concentration, temperature, contaminants or process that changes chemical make-up and so on. Don≈t be quick to accept answers. Explore.

Upon determining exposure characteristics, what will the environment be like before, during and after application? What is the condition of the substrate? Is the substrate acceptable for use under a new surfacing? If not, can the substrate be prepared for use?

If the substrate is not amenable for preparation, can it be rejuvenated by patching or partial replacement? Does the substrate need to be replaced? If so, with what?

What is the time factor? How much time is available from preparation to final cure?

Can the area be made to be environmentally acceptable for an appropriate resinous surfacing within the overall time frame?

If not, how critical is the repair requirement? Can the area be repaired with a system that will fit the environmental time frame, with the knowledge that the repair will not be permanent? How long will the lesser repair likely function? Does the mill want to proceed with the lesser repair knowing that it will be only temporary?

As mentioned earlier, surfacing systems make no exception by industry or environment. Each system has specific environmental and time constraints. We cannot change those requirements.

Perhaps, though, we can effect repairs in smaller sections of the whole area, keeping a small section dry and not interrupt production. Maybe a lesser system could function for a year rather than five, and that condition is acceptable.

If a tile chest is in need of repair and the appropriate repair material is a vinylester or polyester mortar, but only 3 hours is available to make the repair, those systems are not likely to work. By the time the substrate is dried sufficiently for application, the chest has to be back on line.

Perhaps a moisture-tolerant, fast curing novolac epoxy is a better short term choice. At least the system has a chance to function for a while, if only until the next time the chest is down. Mill management must be involved in that type of decision, to assess the overall picture of cost and down-time.

Only substitute a lesser surfacing if it has a chance of performing. There is no point in substituting a material to make a repair if two hours later chemicals will disintegrate it. If a substitute repair cannot be effectively made with a likely chance of short term survival, there is no point in making any repair.

It is incumbent upon specifiers, suppliers and contractors to make mill managers understand the down side of compromise. Repairs are costly when made over and over. Compromised repair materials and methods will ultimately not provide full protection of the substrate and infrastructure. Everyone must understand that compromises can be made for short term protection, but they are not the final answer.

Compromise has its place. If compromised repairs are made with regularity, at frequent intervals relative protection and integrity can be maintained. But, compromised repairs should be investigated as often as possible to ensure integrity and re-repair.

Compromise is, after all, compromise.

Compromise takes its toll. Sooner or later a substrate will become so contaminated or deteriorated that the plant≈s infrastructure will be at risk. Something more permanent will need be done. Only plant management can assess the risk of delay.

Cluster Rule and its Corrosive Effect On the Pulp & Paper Industry

From the Environmental Protective Agency, Fact Sheet November 1997:

> ĄThe combined air and water Ącluster ruleΔ for the pulp and paper industry protects human health and the environment by reducing toxic pollutant releases to the air and water. The technology standards in the rule cut toxic air pollutant emissions by almost 60% from current levels and virtually eliminate all dioxin discharged from pulp, paper, and paperboard mills into rivers and other surface waters. The rule also provides individual mills with incentives to adopt Advanced Pollution Control Technologies that will lead to further reductions in toxic pollutant discharges beyond the water discharge limits set in the rule.
>
> This is the first time EPA has issued an integrated, multi-media regulation (or Ącluster ruleΔ) to control the release of pollutants to two media (air and water) from one industry. EPA is issuing these joint air and water standards under the authority given to them in the Clean Air Act and the Clean Water Act. In doing so, EPA is making it possible for individual mills in this industry to consider all regulatory requirements at one time. This will reduce the regulatory burden on these mills and allow them to select the best combination of pollution prevention and control technologies that provide the greatest protection to human health and the environment.Δ

The Cluster Rule reduced effluent limits for toxic pollutants in the wastewater discharged during the bleaching process and in the final discharge from mills. The limits are based on ***substituting chlorine dioxide for chlorine in the bleaching process.***

Unfortunately, at this writing, no manufacturer has a corrosion-proof surfacing which will withstand long term exposure to chlorine dioxide at elevated temperatures.

Vinylesters were used successfully in the past to protect against bleaching exposures. They are no longer working with that success against chlorine dioxide, especially at elevated temperatures.

Certain polyesters, actually developed with 1950's technology, seem to be holding up better than any other surfacings, but still not satisfactorily.

On-site testing is being conducted by mills where a number of surfacings and sheet good materials have been placed. Interim inspections have shown polyester and some prefabricated thermosetting plastics to be holding up better than other products, but still show evidence of degradation.

Polymer suppliers and formulators are working to solve this dilemma, but no fast answers seem to be on the horizon.

Short term protection against chlorine dioxide, unfortunately, seems to be the ultimate compromise.

Conclusion

Corrosion-proofing in the Pulp and Paper Industry, particularly in a maintenance environment, is a serious challenge. Especially now, operating under stringent environmental guidelines, attention to detail and creativity of specifiers, owners, suppliers and contractors are critical. Understanding behavior of corrosion-proof surfacings and their performance in specific situations are keys to long term, as well as limited success.

Costs for maintenance are high. Costs for lack of maintenance are higher. The need for inspection has never been more important in the Pulp and Paper Industry than it is now. The need for cooperation among specifiers, owners, suppliers and contractors has never been more important than it is now.

Mills will be forced to spend even more money to stay operating, beyond the costs for implementation of the Cluster Rule. The contingent costs of chlorine dioxide≈s corrosive effects may not be fully realized for a long time. Awareness of potential degradation, inspection and maintenance will help alleviate long term corrosion problems.

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