Novel UV Cured Resins for Infield Coating of Concrete, Timber, Plastics and Related Surfaces; a Carbon Trading/Ecological Footprint Analysis of the Process.

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Abstract

The results of novel work utilising the infield UV curing of oligomer/monomer formulations onto concrete and timber are discussed. The technology used is outlined including the advantages and disadvantages of the system, the nature of the polymers utilised and the preferred materials including the incorporation of copolymers of CT complexes because of the very low viscosity and photoinitiator free curing properties of these unique resins. The types of curing lamps are examined and the value of LED systems is considered because of the shielding problems inherent with using mercury lamps. The markets for the process are reviewed, and applications for concrete, timber, plastics and related materials are described. The process is shown to be another very strong example of why UV systems are important for reduction of emissions and energy from coating processes. This conclusion is supported by a carbon trading/ecological footprint analysis. This is the second example of the power of UV systems in this field, the first being presented at the last RadTech USA meeting on the subject of recycling waste banana trees.

Introduction

Coating of concrete, timber, plastics and related materials has been an established process for many years in research, urban, and at industrial sites especially large scale environments. The resin systems most commonly used, especially for timber, are solvent based urethanes with epoxies also relevant especially for concrete. These systems possess a number of environmental disadvantages including relatively high solvent contents which often exhibit occupational health and safety issues, as well as flammability and odour problems. The relatively slow cure of these systems also limits the optimisation of production of finished coated products.

In contrast, the UV process possesses a number of potential advantages which will be outlined in this paper. Currently, UV curing uses line processes in which the resin coated substrate travels on a conveyor belt under a fixed lamp system. Since the 1970's, UV has been successfully used in the graphic arts industry and more recently for coating on fibre-cement and timber boards. A severe limiting problem with the expansion of UV technology into other areas has been the higher cost and often high viscosity of many resins. Many UV formulations were too viscous for application by roller coater (the most commonly used technique), and methods for reducing the viscosity often led to loss of physical properties needed for the coating. These problems have now been essentially resolved and the technology is available for development in other areas such as the one being discussed in this paper.

In addition, new designs in lamp technology have been developed and are available for use in these systems. Such advances permit safer use of the lamps especially in mobile units. The development of LED lamps has great potential in this area and will be discussed. Using such new facilities necessitates more research into new oligomers which will cure under the different lamp conditions, an aspect that will also be examined.

Finally, the boost to the technology may be the climate change concept. The UV process replaces solvent based products and is ideal for reducing the use of energy and reduction of emissions. In this paper, it will be shown that a UV process gives a positive carbon trading/ecological footprint analysis using the appropriate transforms, compared to traditional technologies.

Experimental

The acrylate resins were synthesised by traditional acrylation processes. The oligomers used were acrylated epoxy, polyester and urethanes, both aliphatic and aromatic types being applied. For the concrete work, two urethanes were required since the coated product under certain conditions could be exposed to sunlight. Aromatic urethanes yellow under such conditions whereas aliphatic systems are stable. For the synthesis of certain epoxy and urethane acrylates, novel proprietary technology was utilised. Conventional multifunctional acrylate monomers such as TPGDA and the like were used as diluents as required in the final resin formulations. For some applications, charge transfer complexes of unique structure and typified by maleic anhydride/vinyl ether combinations were also incorporated into the compositions. To achieve the optimum properties in the coatings, conventional additives were included e.g. defoamers, flow additives, photoinitiators and the like.

The basis of a typical formulation is shown in Table 1. The information in the Table will be of particular value to end-users who are not very familiar with UV curing. The important feature of these formulations especially for coating floors is that the percentage of oligomer in the formulation must be as high as possible particularly if urethanes are being used especially for timber substrates. The presence of relatively high percentages of oligomer in the coating means that the finished cured product will possess predominantly the properties of the oligomer rather than the diluent monomer which is not as tough or resilient. Thus difficulties of obtaining oligomers of low viscosity have limited the application of UV technology especially for coating of flooring for a number of years. Oligomers of lower viscosity and also novel CT complexes are now available which only require the incorporation of minimal amounts of diluent monomer to achieve successful application by roller coating at room temperature.

Table 1: Typical Formulation for Coating Concrete/Timber

Component	%
Oligomer, CT complexes	40-60
Monomer	30-50
Photoinitiator/sensitiser	1-6
Additives	0.5-2

A further formulation problem with these UV coating, again relates to the relatively high viscosity, is that it is difficult to include matting agents to control levels of gloss. The problem occurs because as matting agent is added, the viscosity of the formulation increases necessitating the addition of diluent. Recent resin developments have now overcome these problems. In a similar manner, pigmented finishes are more difficult to cure because most pigments are not transparent to UV radiation and thus curing is inhibited. Development of new photoinitiators has again helped to overcome this problem.

There are generally two application techniques for coating of flooring. Firstly, the applicator manually roller coats the whole area to be cured, and then it is exposed to UV. Alternatively, the applicator works with the lamp operator so that immediately after application of the coating formulation, the site is cured. The lamp with power supply can be mounted on a moveable trolley which is manually controlled. The lamps may be either mercury or LED UV sources, but LED has several advantages which will be discussed later.

Before application of the coating the surfaces may need to be pre-treated. Thus for concrete, in some instances, acid etching may be required whereas in other situations light sanding or even a light wash is necessary. The importance of this step is to ensure strong adhesion of the coating to the surface. With concrete, bonding involving strong physical or Van der Waals forces will enhance the properties of the finished film. The presence of inorganic elements in concrete also raises the possibility of formation of coordination complexes with the polymer coating. These complexes may form with many functional groups but especially with urethanes which contain nitrogen lone pairs.

In contrast to concrete, timber is a vastly different substrate for coating using the current technique. In order to achieve strong surface bonding with timber, pre-coating with a sealer material is advantageous in the primary step. This raises the grain of the timber enabling subsequent topcoats to penetrate the wood and form strong bonds. Before applying the topcoat, it is necessary to sand the product to remove the rise in grain otherwise imperfections will be apparent in the final coating. Bonding between the coating and timber is potentially strong because both materials are predominantly composed of organic compounds. Timber has lignin which is aromatic in nature and cellulose is a carbohydrate polymer. Much basic work[1] has been performed on understanding the factors affecting the UV curing of monomers and oligomers onto cellulose and the bonding involved. The following sequence of reactions has been proposed to explain the formation of chemical bonds (as distinct from physical) during UV curing of coatings onto cellulose (CeOH). The coating formulation contains photoinitiator (PI), and monomer/oligomer (M).

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{P}^{\bullet} + \mathrm{I}^{\bullet} \qquad (1)$$

$$\mathrm{P}^{\bullet} + \mathrm{CeOH} \longrightarrow \mathrm{PH} + \mathrm{CeO}^{\bullet} \qquad (2)$$

$$\mathrm{P}^{\bullet} + \mathrm{M} \longrightarrow \mathrm{PM}^{\bullet} \qquad (3)$$

$$\mathrm{M}_n^{\bullet} + \mathrm{CeO}^{\bullet} \longrightarrow \mathrm{CeOM}_n \qquad (4)$$

$$\mathrm{CeO}^{\bullet} + \mathrm{M} \longrightarrow \mathrm{CeOM}^{\bullet} \qquad (5)$$

Reaction 1 creates free radicals required for the polymerisation reactions. Reaction 2 is a curing reaction, but reactions 4 and 5 are grafting reactions. Reaction 4 is a grafting reaction of a polymer radical to a cellulose radical and reaction 5 is cure-grafting in which the polymerisation reaction is initiated at the surface of the cellulose. Both grafting reactions are important because they greatly increase the strength of adhesion of the coating to the cellulose.

From the experiments carried out in this work, the nature of the bonding between the coating and the substrate is extremely important, more so than in graphic arts applications because the coating may be exposed to much harsher conditions such as in warehouses, building sites and the like. For this work, urethane oligomers possess the best properties of all of the oligomers studied.

Discussion of Experiments Performed.

From the UV curing experiments, the following advantages of the technology have become apparent and have been summarised in Table 2.

Speed of cure and freedom from solvents both lead to low odour and these are important for an environmentally friendly coating. This is also important when curing in confined spaces in houses where odours may be released for weeks when traditional solvent-based coatings dry and cure. Large areas such as warehouse floors may be recoated quickly using the UV process. Energy reduction is found for the UV curing compared to traditional solvent based coatings because there is no need for the use of heat lamps to aid in drying of the coating.

Table 2: Advantages of Infield UV Curing of Coatings on Concrete/Timber Compared to Solvent Based Coatings

1. Vastly improve speed of cure
2. No solvents
3. Environmentally friendly
4. Positive carbon trading/ecological footprint results compared with conventional solvent based coatings
5. Capacity to cure larger areas quickly
6. Low odour
7. Ease of recoating over old finishes
8. Energy reduction
9. Ease of work-up
10. Economic advantages
11. Large saving in application times especially for timber
12. Immediate use of the coated surface after curing

In addition to the advantages shown in Table 2, the difficulties shown in Table 3 were overcome in the current research.

Table 3: Current Problems with UV Curing of Coatings on Concrete/Timber.

1. Chemistries available are limited
2. New chemistries required for wider applications
3. Adhesion on some substrates may be difficult to achieve e.g. hardwoods
4. Curing of pigmented systems
5. Heat control in the coatings during curing

Because UV is a relatively new technology, the resin technology available is limited. With the development of a wider variety of oligomers, the technology will expand. Two other problems already briefly discussed are adhesion to some substrates and curing of pigmented systems. Finally a difficulty observed in flooring systems is the control of heat generated during curing of the film. Mobile systems have much lower speeds (about 4 m/min) compared to conveyor lines (100 m/min) so that lamp power and radiant IR of sources needs to be carefully optimised to prevent heating problems for the mobile process.

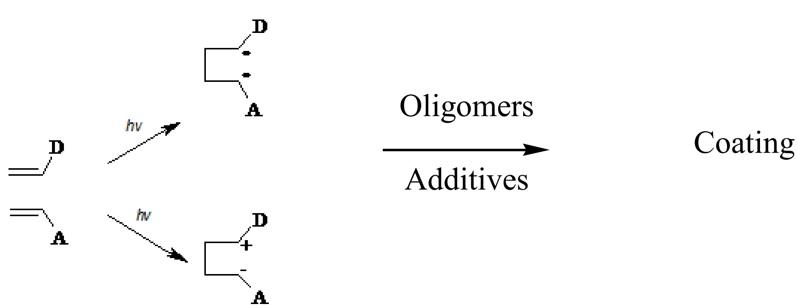
Polymer Systems Used

In the current work, most of the resin systems were acrylated urethanes, epoxies and polyesters. For concrete surfaces, it was found that all of these oligomers could be used but for timber, urethanes were preferred as topcoats particularly the aliphatic urethanes. Compared with concrete, timber flooring has much more movement when under load, thus restricting the oligomers which can be used for this application.

The principal problem in developing formulations was the relatively high viscosity of the oligomers. Oligomers are now available with lower viscosities but charge transfer complexes proposed by Hoyle and Jönsson[2] may be an alternate solution to this problem. These materials possess a number of advantages when used to form copolymers with the oligomers during curing of the coating. Using CT complexes, it is possible to conserve the properties of urethane oligomers but also improve other properties of the cured film. These advantages are outlined in Table 4. An example of a suitable CT system is using vinyl ethers as donors and maleic anhydride as an acceptor (see Reaction 6).

Table 4: Advantages of CT Complexes in UV Curing of Coatings on Concrete/Timber.

1 Very low viscosity
2 Compatible with most monomer/oligomers
3 Compatible with most water-based UV formulations
4 Self curing- acts as a photoinitiator
5 No extra photoinitiator is required which reduces cost
6 Copolymerises with oligomers/monomers
7 No residual photoinitiator remains in the cured coating
8 Relatively inexpensive
9 Cure-grafts readily to cellulose and improves adhesion of the coating to timber.



(6)

Health Aspects of LED Lamps

The mobile UV process must have the lamps well above the substrate and these must be efficiently shielded to minimise exposure of people to the strong UV. On conventional lines using a conveyor belt, the shielding is more efficient than for the mobile unit. This raises an issue of using mercury lamps which have peak intensities about 365 nm for mobile units, but LED lamps optimised to produce radiation at 400 nm may be a solution. Table 5 outlines some of the advantages of this suggestion.

Table 5: Current Advantages of LED in UV Curing of Coatings on Concrete/Timber.

1 Cold cure
2 Minimum heating of coating by IR radiation generated from the lamp which is useful for limiting the temperature of the coating during cure.
3 Main wavelength can be about 400 nm which is relatively safe for eyes
4 10,000 hours lifetime
5 Range of wavelengths available

The LED operate at a much lower temperature and produce little radiant infrared radiation. This is an advantage in controlling the temperature of the coating especially at the lower “line speeds” for the mobile unit. The LED lamps have a long lifetime and can be produced with peak intensities at selected wavelengths. The disadvantage is that most of the chemistries for UV coating have been optimised for curing with mercury lamps. However, our experiments have shown that it is not difficult to adjust formulations to cure coatings on concrete and timber using LED lamps.

Markets

For concrete the potential of the technology is extremely wide. A large number of areas in the building industry are promising for the exploitation of UV curing using mobile units. Currently the technology is being used on flooring in warehouses, supermarkets and aircraft hangers. The unique resin technology is now being used in urban environments in Australia. Concrete floors are given a gloss non-slip UV coating. This is much more economical than other coverings for concrete.

The mobile process is in strong competition with traditional moisture cured urethanes. There is a very strong potential to replace the moisture cured urethanes because the urethanes are solvent based, much slower to cure, and significant amounts of volatile organics are released into the atmosphere.

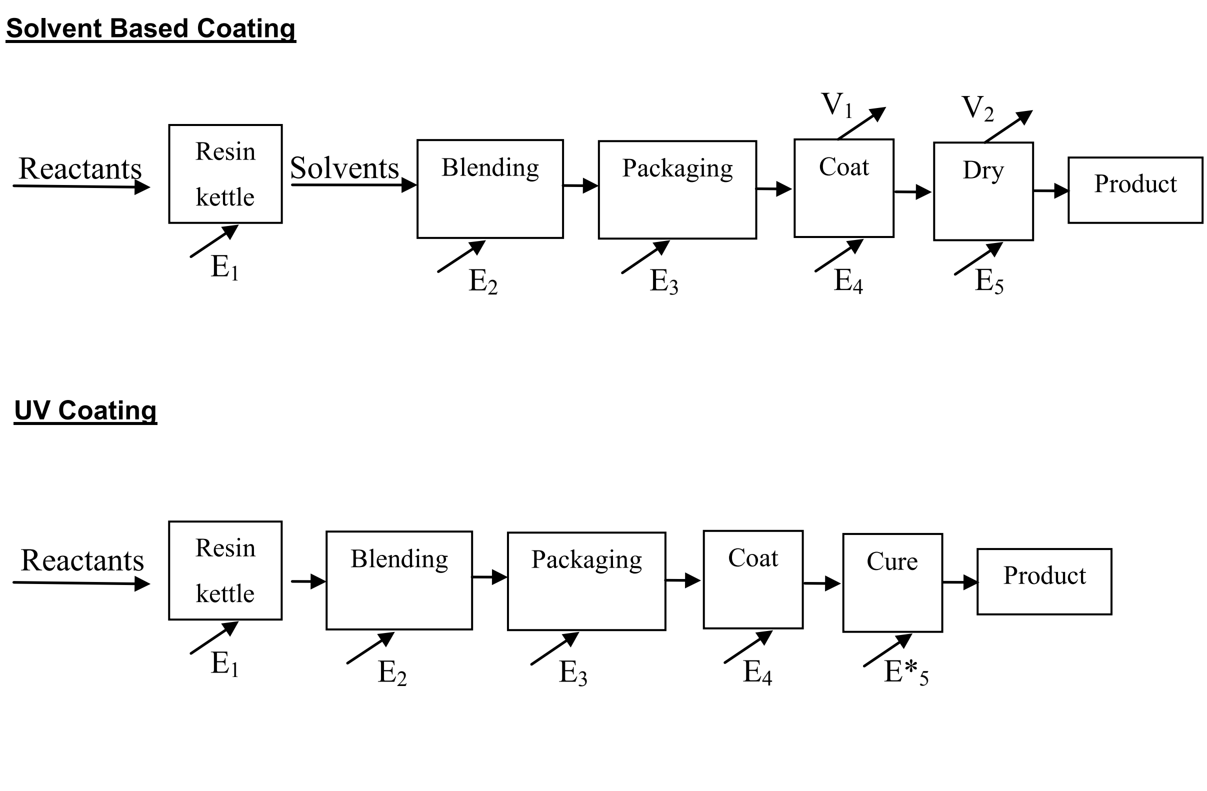
Formulations for softwood have been developed and trials have shown that these coatings have very good mechanical properties. The adhesion of the new coatings to hardwood timber flooring requires some more development work to allow full exploitation of this technology in this application. Extension of the infield UV process to other floor surfaces such as vinyl is also feasible and is one of the projects currently underway.

Evaluation of the Environmental Importance of the Current UV Process.

In the last RadTech USA meeting, an attempt was made to quantify the importance of a UV process using a carbon trading/ecological footprint analysis. This compared a conventional chemical pulping process to produce paper with a UV process using waste banana trees. The current mobile UV system can be compared with the traditional solvent based coating and this analysis is shown in Figure 1. Some factors have not been included in analysis of the solvent-based coatings for example the extra plant space required for storage of solvents, and the limitation that the resin kettle is only utilised to 50% volume for solvent based resins but 80% for UV resins.

The transforms show the exceptional advantages of UV technology which are very relevant to the climate change debate. Although Figure 1 does not show the energies calculated from thermodynamics for the processes, these and the amount of organic emissions could easily be added to give quantitative data on carbon trading/ecological footprint calculations. Even without the quantitative data, the qualitative deduction is that the UV process is superior to the solvent-based technology because it must use far less energy and has virtually zero emissions of volatile organic compounds. Thus companies adopting this technology to replace solvent-based coatings may have an excellent opportunity to claim credits in a new carbon credit/tax trading regime in the future.

Figure 1: Environmental Analysis of Solvent Based Coatings Compared with Infield UV Coatings-Carbon Trading/Ecological Footprint



E_i = Energy, V_i = Emissions, $E^*_5 << E_5$

Conclusions

Work reported in this paper demonstrates the value of infield UV curing in providing a novel process for coating of concrete and timber flooring. The parameters affecting the efficiency of the process were reviewed including the advantages and disadvantages of the system. The coating of concrete is shown to be simpler than timber because of adhesion problems however there is a strong commercial requirement for both systems. The use of novel resin systems including the utilisation of CT complexes as copolymers in the coating is considered. The value of LED lamps to replace mercury lamps is evaluated. A carbon trading/ecological footprint analysis of the process has been performed and the results demonstrate the value of UV systems in the climate change debate.

References

1 G. R. Dennis, J. L. Garnett and E. Zilic, Rad Phys Chem, 67, 391 (2003).

2 S. Jönsson, J. Hulgren, P.E. Sundel, M. Shimose, J. Owens, K. Vaughn, C.E. Hoyle, Proc. RadTech Asia '95, Bangkok, Thailand, 1995, p.283