Advances in the Science and Technology of Paints, Inks and Related Coatings: 2005

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Keywords

Adhesion, VOC emissions, coatings, catalysts for drying of alkyd paints and coatings, transparent conductive coatings, hybrid organic-inorganic coatings, UV curing, biocidal coatings, paints, weathering, wood coatings, surface treatment of concrete, metal corrosion, pigments, film formation, printing, modelling fluid flow in printing, dot gain, inkjet printing

Summary

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This review summarises the developments in adhesion, VOC emissions, coatings, transparent conductive coatings, hybrid organic-inorganic coatings, UV curing, biocidal coatings, paints, weathering, wood coatings, surface treatment of concrete, metal corrosion, pigments, film formation, printing, modelling fluid flow in printing, dot gain and inkjet printing reported in *Surface Coatings International Part B: Coatings Transactions*, **88**, 2005.

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Adhesion

A useful surface coating must not only adhere to its substrate, but must also cohere to itself. However, at present there is no satisfactory molecular theory which can be used to predict the interaction of two materials across their mutual interface. In a very informative and major detailed review, Peterson has pointed out that all existing theories of adhesion assume that a part of the molecular interactions involved obey the London inverse-sixth power law which is valid for the separations involved in gases.[1] However, it has been shown that the London law is invalid both for the Casimir limit of large separations and for the close molecular contact that occurs in condensed phases.[2]

Peterson asserts that because of its complexity in the disordered condensed state, modern quantum theory provides no indication of regularities out of which a predictive formula could be developed.[1] As a result, recourse to the empirical approach is all that currently remains. Following a review of the experimental data on molecular interactions, the Szkyskowski formalism was developed[3] and was shown to explain the temperature dependence previously observed by Vrbanac and Berg.[4]

The most successful approach to describing the interfacial interactions of general materials is that of van Oss, Good and Chaudhury.[5] In their model, the interactions are considered to be London dispersion and undifferentiated Lewis acid-base interactions. This approach has been shown to be valid under various simplifying assumptions. However, in order to develop it as a theory providing significant predictive power, Peterson proposed that it must be modified in three aspects.[1] These are, firstly, that an additional parameter is required, and then the theory must be modified by using non-linearity, and by a separate consideration of entropic terms.

The majority of tests used in the coatings industry to assess adhesion are destructive and difficult to correlate with performance. In addition, destructive tests are incompatible with best practice in inspection and quality control. While adhesive performance tests on coatings are usually expressed as a failure limit and cannot be measured non-destructively, Graystone and Kennedy have pointed out that it is possible to assess the factors which contribute to adhesive performance independently of true molecular adhesion.[6] Among such factors, they include the presence of flaws or poor contact, mechanical properties, including the modulus of elasticity, or a sensitivity to environmental factors, including the ingress of moisture. These and other factors, it is asserted, can be assessed by 'non-destructive adhesion testing' (NDAT).

Graystone and Kennedy have summarised the principles of operation and features or constraints of a number of NDAT methods,[6] namely:

- acoustic emission;
- electrochemical impedance spectroscopy (EIS);
- localised EIS (EIS);
- electronic speckle pattern shearing interferometry (ESPSI);
- micro hardness tester;
- micro scratch tester;
- scanning acoustic microscopy;
- scanning Kelvin probe microscopy;
- pulse thermography;
- ultrasonic force microscopy; and
- ultrasonic techniques.

Three techniques were selected for preliminary investigation, namely acoustic emission, pulse thermography and electronic speckle pattern shearing interferometry. It was concluded that all of these techniques were capable of investigating different aspects of adhesive failure.[6] For example, pulse thermography could detect sub-surface damage not apparent to visual inspection. Acoustic emission, under some circumstances, could give information of damage initiation prior to catastrophic failure. ESPSI was also shown to be capable of detecting sub-surface damage, and, moreover, also showed promise for the detection of differences in strain transfer prior to any detachment failure. NDAT methods may thus prove useful in the search for novel coatings with enhanced adhesive performance and in assessing adhesion failure.

Approaches to decreasing VOC emissions in paints and coatings

Solvent-borne coatings have been widely used, but environmental pressures to limit the release of VOCs (volatile organic compounds) into the environment have stimulated alternative approaches such as water-borne binders (eg latex dispersions or alkyd emulsions). While latex dispersions possess small particle size, fast-drying and good outdoor durability, their levelling is generally not good and the open time is considered too short. Alkyd emulsions, on the other hand, have a lower molecular mass at the moment of application compared with a polymer latex, and hence this can be of great benefit for good penetration, adhesion and gloss.

Hybrid systems containing both acrylic latex dispersions and alkyd emulsions have been studied by Deriss and Karlsson to obtain binders with optimal characteristics.[7] A number of high-solids (80%) acrylic latex-alkyd emulsion hybrid binders were prepared using a linseed oil alkyd with a molecular weight (Mw) of 7,300g/mol, an oil length of 75%, and one butyl acrylate-co-methyl methacrylate latex (T_g 19°C). A mixture of non-ionic surfactant and an anionic surfactant were used in experiments where extra surfactant was used. A dryer (siccative) was added as 0.05wt% Co to the alkyd prior to hybrid preparation and film preparation.

The film morphology during the drying process was studied using optical microscopy, and the morphology of the alkyd-acrylic hybrid samples was examined using a transmission electron microscope (TEM), the residual double bonds in the alkyd being previously stained using osmium tetroxide.[7] Atomic force microscopy (AFM) was used to study both the morphology and topography of the hybrid film surfaces.

The liquid structures of the hybrids consisted of alkyd droplets dispersed in an acrylate dispersion matrix.[7] By varying the preparation method, surfactant concentration and pH, the liquid structure could be changed from a single o/w (oil in water) emulsion to double or multi w/o/w emulsions. The film morphologies of the hybrid systems showed that the liquid morphology was preserved on a macroscopic scale during film formation. At the microscopic scale, AFM and TEM analysis revealed the presence of an alkyd phase between the latex particles. An important observation was that the VOC emissions of paints made from the alkyd-acrylic hybrid system were lower than 10μg/m²h which is the value recommended by the Asthma and Allergy Society of Sweden.

Another promising approach to decreasing VOC emissions in paints and coatings is to replace some or all of the solvent with a reactive diluent that becomes part of the film matrix on curing.[8] Reactive diluents must be capable of dissolving the polymeric binder either entirely or to a significant extent. The resulting solution must then have a viscosity suitable for commonly used application techniques (eg spraying, brushing etc).

Fatty acid ester diluents have been used with alkyd polymers but are subject to hydrolysis which can affect the viscosity.

Berry-Walker et al have used oxazoline derivatives of fatty acids as reactive diluents for the mixture of fatty acids in tall oil (mainly linoleic acid).[8] The polymers obtained had relatively good solubility in the oxazoline derivative and solutions with moderate viscosity were obtained. At ambient temperature, films made from the polymer solution showed little property development. However, when cured at elevated temperatures (eg150°C), good properties in respect of solvent resistance, hardness and gloss were obtained, but this depended upon the time that the films were held at the elevated temperature.

Catalysts for drying of alkyd paints and coatings

Cobalt carboxylates (eg cobalt (II) 2-ethylhexanoate) are the most effective, commercially-available catalysts for the oxidative drying of alkyd paints,[9] but are suspected to be carcinogenic to tissues and lungs.[10] Manganese-based catalysts (eg manganese octoate) are available, but their catalytic activity is reported to be much lower than the Co-based catalysts.[9]

A dinuclear manganese-based complex, namely, $[Mn^{IV}_2(\mu\text{-}O)_3L_2](PF_6)_2$, termed (MnMeTACN) – where L is 1,4,7-trimethyl-1,4,7-triazacylclononane – is claimed to be an active catalyst for ethyl linoleate (EL) both in solutions and for EL emulsions.[11] While EL may be considered as a model compound for alkyd coatings, Oyman et al point out that only oligomers are formed with EL during oxidation, whereas a cross-linked network is created during drying of the alkyd.[11] This greatly increases the viscosity and the resultant immobilisation of polymer chains could have a significant effect on further reactions.

Accordingly, Oyman et al have studied the chemical changes during the drying of several solvent-borne and water-borne alkyd coatings, for both of which MnMeTACN has been found to be a suitable catalyst and a potential alternative to the commercially-available Co- and Mn-based catalysts.[11] The depth profile of the drying process for alkyd coatings was followed using Confocal Raman microscopy (CRM) to follow the C=C double bond conversion in the deep layers of the coating films. It was demonstrated that slow surface drying is somewhat compensated by relatively fast deep layer drying, so that the catalytic activity of MnMeTACN appears to fall in between those of the commercial Co- and Mn-based catalysts.

Siloxane-acrylic coatings

Exterior decorative coatings are widely used in construction and building materials, and siloxane-acrylic copolymers can meet the requirements for these end-uses. Zhang and Yang have prepared siloxane-acrylic latex by simultaneous free-radical and condensation reactions between acrylates and polysiloxanes using batch and semi-continuous processes which mainly affected the dry time of the resulting coatings.[12]

It was demonstrated that the siloxane-acrylic coating properties, prepared with core-shell morphology particles by the semi-continuous process, were not significantly improved compared with those produced by the batch process.[12] The coating properties, especially the weatherability (determined from the gloss retention after outdoor exposure and UV resistance tested according to Chinese Standard GB1865) and stain resistance tested and evaluated according to Chinese Standard GB9780, were shown to be strongly dependent upon the silicone content. In particular, where the silicone content of the monomers exceeded 8%, the resulting coatings proved to have excellent weatherability and stain resistance, rendering such coatings suitable for application as exterior decorative coatings.

Phenolic epoxidised polyurethane coatings

A recent communication by Shakeb has been concerned with the production of phenolic epoxidised polyurethane (PEPU) coatings, using 60% acetic acid to produce epoxidised linseed oil.[13] Phenolic epoxidised resin was produced by reaction with phenol, and this product was then reacted with toluene diisocyanate to produce phenolic epoxidised polyurethane. The PEPU resin had excellent adhesive properties, and it was found that it could be used as a one-layer coating for petroleum tanks, being applied much more easily and cheaply compared with a previous three-layer coating. PEPU resin coatings with an NCO/OH ratio of 5 were considered to be the most suitable for petroleum tank coating.

Epoxy resin coatings

Commercial epoxy resins are used as monomers for the prepolymers that further react with curing agents to yield high-performance thermosetting plastics and have gained wide acceptance in protective coatings. The most widely used epoxy resins are based on digly-

cidylethers of bisphenol A derived from bisphenol A and epichlorohydrin. Shukla et al have investigated the possibility of decreasing the cost of the epoxy resin and of the polyamide resins by introducing castor oil without greatly affecting the beneficial properties of epoxy-polyamide or epoxy-polyamine systems.[14] It was agreed that the apparent flexibility of the epoxy resin could then be increased substantially with only minor effects on the viscosity and all the other properties of the epoxy-polyamide system.

From the work carried out, it was concluded that blending of castor oil in epoxy resins was possible in limited proportions.[14] Further, the blending of castor oil in polyamide resins (used as an epoxy hardener) could be carried out up to a certain proportion. It was observed that castor oil-modified epoxy resin cured by polyamines exhibited good impact strength. However, the coatings were not transparent. The castor oil-modified polyamide systems were shown to provide a suitable potlife and improved some physical and chemical properties of the epoxy resin.

Direct fluorination of polyethylenes

Direct fluorination enhances the barrier properties of industrial polymers through surface modification, and Kharitonov et al have reviewed the kinetics and mechanism of the direct fluorination of polyethylenes.[15] Their experimental findings on two types of low-density polyethylene (LDPE), five types of high-density polyethylene (HDPE) poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVDF) have been reported.[15] They conclude that fluorination of LDPE and HDPE is a diffusion-controlled process, proceeding via a branched chain mechanism following an induction period.

The reaction initiation proceeds via the reaction of molecular fluorine with the C-H bond.[15] Interestingly the rate of fluorination of HDPE significantly exceeds that of LDPE, which is almost identical to that of PVF. By contrast, PVDF cannot be fluorinated even at temperatures as high as 430K and/or under UV-irradiation. Kharitonov et al also studied the kinetics associated with the formation and termination of peroxy RO-$_2$ and fluorocarbon long-lifetime radicals, and concluded that it is mainly middle peroxy radicals that are formed at treatment conditions close to those used in industrial processes.

Hyperbranched polymers

Hyperbranched polymers (HBP) can be prepared via a one-step polymerisation process and can be used in polymer blends or as additives in linear polymers.[16] Their special branched structure allows HBP to act as rheology modifiers. The HBPs are assumed to disrupt the local entanglement network and decrease the entanglement density of high molecular-weight linear polymers by virtue of their relatively compact globular structure.[17] HBPs are also considered to migrate to the surface to form a lubricating layer which leads to a decrease of the viscosity by either cohesive or adhesive failure (slip) at the surface, or both.[18]

Grundke et al have studied the surface properties of hydroxyl-terminated aromatic-aliphatic hyperbranched polyesters partially functionalised with short alkyl chains.[16] These were considered to have potential as surface tension modifiers or as compatibilisers in polymer blends. The use of thin fibres as solid probes in a modified Wilhelmy balance technique was used to study the effects of HBPs in polyols.

Hyperbranched polyesters P-OH were prepared based upon the monomer 4,4-bis(4-hydroxyphenyl) valeric acid and mixed with an oligo (ester diol) based on phthalic acid, monoethylene glycol and diethylene glycol in a ratio of 1:10.[16] Blends containing 10 and 20wt% of an hydroxy-terminated hyperbranched polyester P-OH had a higher surface tension compared with the pure oligo(ester diol). Even 1wt% of a hyperbranched polyester modified with short alkyl chains (eg methyl, tert-butyl) decreased the surface tension of the oligo (ester diol) by up to 30%. Indeed the surface tension of the modified hyperbranched polyesters equalled the surface tension of the pure modified hyperbranched polyesters. This was taken as evidence that the HBPs were surface-active substances that were located in the surface region of the polymer blend, and this was subsequently confirmed by high-resolution x-ray photoelectron spectroscopy.

Water-repellent coating to prevent surface contamination

Surface contamination can cause the deterioration of the water-repellent properties of coatings applied to mobile phone microphones. Yamauchi et al have reported much improved durability of these properties and of the mobile

phone by applying a specially formulated water-repellent coating.[19] This based upon low molecular-weight poly(tetrafluoroethylene) (PTFE) particles, anatase-type photocatalytic TiO_2 nano particles, fluoro oil (perfluorinated polyether) together with a polyvinylidene fluoride binder. In this way, a water contact angle of more than 150° can be obtained. The photocatalytic activity of the TiO_2 nano particles also inhibits the surface contamination which had previously caused a deterioration of the water-repellent properties. The acoustic characteristics of the mobile phone microphone are maintained by using this coating.

Transparent conductive coatings

Transparent conductive layers are generating considerable interest for industrial applications such as low emittance coatings, heat mirror coatings, radiation shielding, transparent electrodes, electrostatic and antistatic coatings and gas sensors.[20] Indium tin oxide (ITO) is one of the more interesting of the various known transparent conducting oxides, but conventional chemical deposition methods require relatively high substrate temperatures ($>300°C$).[21] Polymeric substrates, pre-formed glasses or devices based on amorphous silicon can thus be seriously degraded either during the deposition process or during post-annealing. Use of low-temperature chemical deposition using sols that are adequate for high-temperature processing gives rise to non-adhesive layers or in soft, easily scratched layers.

A novel approach adopted by Al-Dahoudi and Aegerter has been to separate the crystallisation step of ITO materials from the process of film formation.[21] Crystalline nano-particles of ITO have been prepared and then redispersed in different lacquers. The dispersion of 25nm average size (cubic In_2O_3 structure) crystallites of ITO was carried out by milling in a viscous matrix of ethylene glycol and a dispersing agent. The ITO paste (70 to 75wt% ITO nano-particles) was dispersed under stirring in, for example, ethanol. The blue suspension was centrifuged at 4500rpm for ten minutes to remove the larger aggregates and filtered through a $0.45\mu m$ filter. Addition of different amounts of pre-hydrolysed 3-methacryloxypropyltrimethoxysilane (MPTS) was followed by mixing for five minutes in an ultrasonic bath to produce ITO suspensions stable against aggregation for several months. These could be applied by spin coating, dip coating,

spray coating and web coating techniques.

It was found that the layers transmitted more than 87% in the visible range and acted as infrared-shielding coatings for $\lambda > 1.5\mu m$.[21] The intensity of solar light (Air Mass (AM) 1.5 Global solar spectrum) was effectively decreased, while the layers acted as UV blockers for wavelengths less than 400nm, thereby protecting polymer substrates and foils from degradation under UV irradiation. The high conductivity ($\sigma \sim 1100Sm^{-1}$) imparted useful electrostatic and antistatic properties as well as for transparent conducting coating with sheet resistance higher than a few $k\Omega_\square$. An encouraging factor for their use was their excellent adhesion on all substrates, together with high abrasion resistance and weathering resistance.

Lower critical solution temperature (LCST) polymer coating

The coating of a solid substrate with an organic polymer coating is normally achieved using polymer adsorption, polymer grafting or polymer deposition/precipitation. Eisenbach et al have reported on a novel variant of achieving an organic polymer coating by precipitation, by using the technique of thermodynamically-controlled precipitation.[22] This is based upon the critical phase behaviour of polymer solutions. Thus, a polymer may become insoluble when a certain temperature – the so-called lower critical solution temperature (LCST) – is exceeded. Similarly when the temperature falls below a critical value, the upper critical solution temperature (UCST), phase separation occurs.

The utilisation of this LCST behaviour has been employed by Eisenbach et al to coagulate and precipitate poly (oxyethylene – block – oxypropylene – block – oxyethylene) block copolymers and poly (N-vinylcaprolactam) on to SiO_2 wafer surfaces.[22]

It has been demonstrated that LCST polymer coating technology not only allows a controlled surface modification of pigments or flat substrates by an organic polymer coating layer, but also allows the introduction of specific surface features of nanoscopic (around 100nm and below) to mesoscopic (sub-μ to several μ) dimensions. Thus the surface topology may be reversibly varied from a regular, almost close-packed, mesoscopic hemisphere texture to a nanoscopic roughness, or alternatively rendered evenly smooth. Clearly the

LCST application technique opens up new perspectives in the field of smart coatings.

Ultrasonic atomisation of ink

For continuous automatic application of coatings, the technique of spraying using compressed air to atomise the liquid into a fine spray has been widely used. Atomisation can also be carried out using an ultrasound atomiser, and Gaikwad et al have studied the ultrasonic atomisation of ink which was sprayed vertically downwards on to a paper which was moved laterally.[23]

It was observed that the percentage area of the covered surface increased, but the liquid film thickness on the coated surface decreased with an increase in the height of the ultrasound atomiser from the paper surface. Increasing the vibrational amplitude of the atomiser had the same effect. Increasing the linear velocity of the paper surface also decreased the liquid film thickness on the coated surface. Increasing the liquid flow rate increased both the percentage area coated and the liquid thickness. The latter was also increased by an increase in the liquid viscosity, but this was accompanied by a reduction in the area covered by the spray for surface coating.[23]

Polymeric antioxidants for paints

Malshe and Elango, in a recent communication, have prepared polymeric antioxidants based upon p-cumyl phenol formaldehyde resin (PCPF), p-nonyl phenol formaldehyde resin (PNPF) and p-octyl phenol formaldehyde resin (POPF).[24] The reactions were monitored by thin layer chromatography (TLC) and the melting points of the products were determined by the open capillary method.

The effectiveness of these polymeric antioxidants was confirmed by determining their stabilising action in protecting paint against thermal oxidation using a QUV weatherometer. Paint gloss, whiteness and yellowness were evaluated and compared against paints commercially available in India. It was concluded that these low-cost polymeric antioxidants provided better protection against thermal ageing and UV degradation than the standard antioxidants used in commercial paints.[24]

Paint film formation determined by diffusing wave spectroscopy

An adequate, reliable assessment of the rheological behaviour of thin films while drying is an important requirement for contemporary paint research. A recent communication by Breugem et al has studied the use of diffusing wave spectroscopy which, in contrast to conventional mechanical tests, avoids the paint film becoming damaged or modified during the test.[25]

Diffusing wave spectroscopy is an optical technique that is based upon the characteristic changes with time in the light scattered off the drying paint film. It is a non-invasive technique applicable, in principle, to all paints containing particulate matter at length scales comparable to that of light, of the order of $1 \mu m$, such as alkyd resin emulsions and latex dispersions. Diffusing wave spectroscopy was originally used to study the dynamics of complex fluids such as strongly scattering media.[26,27]

Temporal fluctuations in the scattered light are directly related to the motion of particulate matter inside the fluid. The temporal motion of particles is related to the viscoelastic moduli of the system which is extracted using a generalised Langevin equation with a memory kernel.[28] Breugem et al applied the method to the drying of alkyd resin emulsion films and demonstrated that it is possible to extract viscoelastic information and accurate temporal information on the drying process.[25] The elastic modulus and high-frequency viscosity parameters measured are low-shear parameters and are not directly related to high shear values, although in general there are strong correlations between these quantities.

Hybrid organic-inorganic coatings

There is currently much interest in organic-inorganic hybrid materials for many applications in surface coatings. This is because it is possible to combine, on a nanometric scale, inorganic moieties (with high modulus, thermal stability and low coefficient of thermal expansion) with organic oligomers or polymers that possess high ductility and may be processed at low temperature.[29] Of the many methodologies available for the preparation of such materials, the sol-gel process is often preferred because of the mild conditions required.

Messori et al have prepared hydrophobic-oleophobic coatings via the sol-gel

process with organic-inorganic hybrids based on perfluoropolyether-polycaprolactone (PFPE-PCL) copolymers.[29] A number of coatings were prepared by varying the organic-inorganic ratio, the PFPE/PCL ratio in the copolymer and the reaction conditions, and coating on to glass substrates. Surface characterisation was evaluated using contact-angle analysis and x-ray photoemission spectroscopy (XPS). For all the samples studied, the wettability was very low and the surface composition analysis demonstrated that the surface segregation of the PFPE segments was always high enough to impart a very high hydrophobic character to the surface of the coating.

Hybrid organic-inorganic nanocomposite materials formed by the sol-gel process have been considered to rank among the most progressive polymer products developed over the last two decades.[30] Unique products with specific functionality can be prepared to provide protection against abrasion, corrosion, hydrolysis and oxygen, as well as generating scratch-resistant properties.

Spírková et al have described the preparation and characterisation of hybrid coatings formed from a functionalised organosilicon precursor, diethoxy [3-(glycidyloxy)propyl] methyl silane (GMDES) and an oligo (oxypropylene) triamine (Jeffamine T403) (T403) in the presence of two nano-additives (colloidal silica, montmorillonite).[30] The properties of the hybrid coatings prepared from GMDES-T403, GMDES-T403-silica, and GMDES-T403-montmorillonite (MMT) were then compared using optical microscopy, atomic force microscopy, nuclear magnetic resonance (NMR) spectroscopy, dynamic mechanical thermal analysis, wide-angle x-ray scattering (WAXS), transmission electron microscopy (TEM), and also by tensile characterisation.

The surface morphology of the hybrid organic-inorganic coatings was found to be very sensitive to the method of preparation and to the type of nano-additives used.[30] Coatings prepared without any nano-additive or in the presence of colloidal silica showed a practically uniform surface relief. However, the MMT particles self-assembled and formed clusters of various shapes and sizes, and hence in surface relief, worm-like formations were observed to be more evident with products with MMT dispersed in water. The montmorillonite was observed to be partially intercalated, partially exfoliated. Montmorillonite did not influence the overall degree of polyaddition (0.95 to 0.98), but the segmental dynamics differed in both types of final products. MMT gave

rise to differences in the geometry and in the rate of high amplitude motions. However, the addition of ca 1wt% of montmorillonite had little effect upon the tensile behaviour, which was not the case with 20wt% of colloidal silica.

UV curing by radical and cationic photoinitiation

In a major review, Decker has discussed the light-induced polymerisation of multifunctional monomers, which is considered to be the most effective method of transforming almost instantly a solvent-free liquid resin into a solid, highly resistant polymeric material.[31] Specific advantages include cure speed, low energy consumption, low emission of volatile organic compounds (VOCs), and operation at ambient temperature. These advantages are now widely exploited in the graphic arts and coating industries for surface protection of materials by fast-drying varnishes, lacquers or printing inks.

For acrylic resins, a radical mechanism is involved, whereas for epoxides, the photoinitiated polymerisation proceeds via a cationic mechanism, the monomers and oligomers designed to possess several functional groups that are converted within seconds into a hardened three-dimensional polymer network.[31] The ultra-fast reactions that take place in the liquid-to-solid phase change can be followed by the use of real-time infrared (RTIR) spectroscopy, enabling the direct recording of conversion versus time curves in a millisecond timescale for coatings exposed to UV or visible radiation.

Under circumstances where the illumination may be insufficient to obtain efficient curing, dual-cure systems have been developed. In addition to the photoinitiator, a functionalised oligomer or prepolymer that will ultimately form the backbone of the three-dimensional polymer network and a monomer used as a reactive diluent to adjust the viscosity of the formulation, dual-cure systems must contain some additional functionalities. These are typically isocyanates and hydroxy groups incorporated to ensure effective cross-linking in the dark areas upon heating.

Radical-type photoinitiators usually consist of aromatic ketones which can generate free radicals upon exposure to UV radiation, either by homolytic cleavage of C-C bonds or by hydrogen abstraction from an H-donor molecule. A large number of commercially-available photoinitiators have been surveyed[32] and an

extensive compilation of monomers and oligomers used in UV radiation curing has been published.[33]

To cure thin coatings in the presence of air and get a tack-free surface-intense illumination is required in order to rapidly consume the oxygen dissolved in the sample and to shorten the exposure time during which air can diffuse into the coating. Atmospheric oxygen reacts readily with free radicals to yield inactive peroxy radicals, inhibiting UV curing of acrylate-based resins. However, this can be avoided where a polyene and a multifunctional thiol are used. Copolymerisation occurs upon UV exposure by a step-growth addition mechanism, but a polymer network requires that both monomers contain more than two reactive functions. Any peroxy radicals formed by O_2 scavenging are capable of propagating a chain reaction by hydrogen abstraction from the thiol and generation of the chain carrier thiyl radical.[31]

However, the higher cost, restricted choice of monomers and unpleasant odour of the formulation has limited the wider use of polyene thiol systems. A further problem is the presence of hydroperoxides in the UV-cured polymer which could affect the long-term stability.

The less widely used cationic polymerisation of multifunctional monomers and oligomers bearing vinyl ether or epoxy groups possesses some advantages, for example lack of inhibition by atmospheric O_2, post-polymerisation in the dark after UV exposure, low shrinkage, high mechanical performance after UV curing, and good adhesion to many substrates, especially metals.[31] Photoinitiators based upon arylsulphonium $(Ar_3 S^+PF_6^-)$ and aryliodonium salts $(Ar_2I^+SbF_6^-)$ are used to generate the protonic acid used to produce ring-opening of epoxides, the cycloaliphatic diepoxides being more reactive than aromatic diepoxides. Marked acceleration of the polymerisation is effected by the addition of a vinyl ether comonomer (eg the divinyl ether of triethyleneglycol).

Where both radical type and cationic type photoinitiators are used to polymerise monomer blends (ie a mixture of multifunctional monomers), the result is a build-up of two interpenetrating polymer networks (IPN). RTIR spectroscopy can be used to follow the photopolymerisation of each monomer quantitatively in real time. The UV curing of monomer blends extends the range of properties that can be attained.[31]

Dual-cure systems can be used where complex shapes or thick pigmented coatings are to be UV-cured.[31] Thermal treatment of a thermally-curable functional group (usually an isocyanate associated to an alcohol), immediately followed by UV exposure of the hot sample, is claimed to achieve the most complete curing system. A photo-curable functional group (usually an acrylate double bond) is then cured using a heat-resistant photoinitiator (eg acylphosphine oxides).

Some observations upon the applications of UV-cured coatings together with a brief review of the effects of the cross-linked resin structure upon its performance and properties (eg hardness and flexibility, and resistance to chemicals, water and weathering) have also been summarised in this informative review.[31]

Interaction of UV light with a suitable photoinitiator can give rise to both radical and cationic species which can be used to cure suitable monomers and oligomers.[34] Cationic photopolymerisation is now receiving renewed interest because of some advantages over radical photopolymerisation among which lack of oxygen inhibition, low shrinkage and good adhesion properties have been cited.[31,34] In addition, the monomers used are generally perceived to be less toxic and irritant compared with the acrylic and methacrylic resins employed in radical processes.[35]

Epoxides can be photopolymerised by cationic species, but sometimes these systems lead to low flexibility and impact resistance. Sangermano et al have studied the cationic photopolymerisation of epoxy systems using Fourier transform infrared (FTIR) spectroscopy.[36]

In order to increase the epoxy conversion and the kinetics of curing under a Fusion lamp (H-bulb) with a radiation intensity at the sample surface of about $280W/cm^2$, alcoholic additives (15mol% of ethanol, isobutanol and tertiary butanol) were introduced into the photo-curable formulations.[36] In the presence of the alcoholic additives, the carbocationic growing chain is terminated by reaction with the hydroxyl group. An ether linkage is formed and simultaneously a proton is produced which then can initiate a new polymer chain. Complete epoxy conversion occurs in the presence of tertiary butanol, but all the alcoholic additives markedly increase the kinetics of cationic photopolymerisation.

The results can therefore be interpreted in terms of a chain-transfer reaction with a flexibility within the network and

increases in the curing rate. It was shown that in the presence of epoxy-hydroxyl-functionalised polybutadiene, the T_g values of the cured films decreased sharply, confirming the strong flexible effect, together with an increase in toughness.[36]

Network non-isocyanate polyurethane coatings

Conventional monolithic polyurethanes have good mechanical properties, but their porous nature, poor hydrolytic stability and insufficient permeability are distinct disadvantages. In addition, the use of toxic components (eg isocyanates) creates additional problems for polyurethane production processes.

Figovsky et al, in a recent communication, have pointed out that network non-isocyanate polyurethanes (NIPUs) are formed as a result of the reaction between cyclocarbonate oligomers and primary amine oligomers.[37,38] This reaction forms an intra-molecular hydrogen bond through the hydroxyl group at the β-carbon atom of the polyurethane chain which increases the chemical resistance by 1.5 to 2 times more compared with materials of a similar chemical structure without such bonds.

Figovsky et al report on the synthesis of novel types of network non-isocyanate polyurethanes (NIPUs) based upon acrylic and siloxane cyclocarbonates and dendro-polyfunctional siloxane primary amine oligomers.[38] In this way it should be possible to develop high-level UV-stable coatings based upon acrylic-dendro-amine systems that are curable at room temperature. Siloxane-based systems have been developed using this approach that exhibit good adhesion and mechanical properties.

This new generation of protective coatings can be used to provide extremely high resistance to solvents, water, acids and bases, as well as providing high adhesion to ferrous and non-ferrous metals.[38] Additional hydrolysis of organosilane oligomers creates a nano-structured network polymer. Interpenetrating polymer network structures can be formed consisting of a polymerised resin network with a polysiloxane network formed by the hydrolytic polycondensation of silane groups. In addition, nanocomposites can be produced by introducing compounds that can form nano-particles in situ such as organosilanes and tetraethylorthosilicate within a three-dimensional polymer matrix.

It is envisaged that preparation of thermo-stable compounds could be achieved using polyhydroxyurethane instead of blocked diisocyanates.[38] Further work is required to determine the coating properties and weatherability performance, and to investigate in more detail the nano-structure of polymers produced using new methods of synthesis.

Biocidal coatings

The versatile sol-gel technique, which is performed at room temperature, creates the possibility of incorporating almost any organic substance, for example oils, drugs, polymers, biomolecules, and inorganic or organic biocides, into the sol-gel matrix to give controlled release effects.[39] The respective constituents may be added either before or after hydrolysis of the silica precursors.

The inorganic sol-gel matrix, prepared by coating with nanoparticle silica sols (nanosols), offers many desirable properties if combined with biocidal systems.[40] In particular, controlled release systems offer the greatest opportunities for variations because inorganic biocides (eg Ag, Cu or boric acid) as well as any organic biocide can be embedded. Further, different combinations of biocides can be co-immobilised to enhance the antimicrobial effect and diminish the resistance risk.

The controlled release of biocides can be regulated by one of three different methods,[40] namely:

- by changing the silica-to-biocide ratio;
- by the use of additives such as alkyl-silanes, polymers or pore-forming, leachable saccharides which change the sol-gel layer structure; and
- by the addition of complex-forming reagents which ensure that the biocide is fixed within the matrix (eg added polyols for the controlled release of boric acid).

Haufe et al demonstrated that the release of boric acid can be controlled for the protection of wood against fungi and insects by simultaneously embedding complexing agents such as polymeric polyols (eg hydroxypropylcellulose).[40] Total inhibition of growth by Coniophora puteana was achieved together with 100% mortality in the termite test and no decrease in mass in either test. Clearly these composite coatings offer great potential as ecologically beneficial wood preservatives because of the high antimicrobial activity and low leaching rates combined with the low antimicrobial ecotoxicity of the components.

Antimicrobial coatings of textiles using silica coatings containing silver combined with biocidal quaternary ammonium compounds such as octenidine or cetyltrimethyl ammonium bromide were compared with polymeric cationic biocides embedded within the silica coatings.[40]

Embedding 30% chitosan within silica improved the wash-out ability and stabilised the optimum biocidal pH range of 5. Using 20%wt of a silane with a 3-(octadecyldimethylammonium)propyl pendant group cohydrolysed with tetraethoxysilane ensured the biocidal ammonium group was covalently bound to the silica matrix.

All coatings showed sufficient biocidal activity against fungi, gram-positive (B subtilis) and gram-negative micro-organisms (E coli). However, with the exception of the chitosan-containing silica coating, a long washing procedure (8 hours, 40°C, 1% sodium dodecyl sulphate with stirring) caused a decrease in biocidal activity. All coatings imparted sufficient protection to textiles against non-specific air germs, an important parameter for textiles.[40]

Silica coatings with embedded silver nanoparticles combined with a tuned mixture of biocides and antibiotics enabled long-term antimicrobial protection of medical catheters due to the delayed release of silver ions from the nanoparticles.[40]

Volatile biocidal compounds (VBCs) can be embedded into sol-gel coatings and released slowly into the gaseous phase, and hence, without a direct contact, the surface of the materials can be protected against biocontamination. Selected substituted cinnamates and phenols are suitable VBCs, but the release of the embedded VBCs decreases with decreasing vapour pressure and/or steam volatility of the VBCs, increasing the mass ratio of silica biocides, layer thickness, and the molecular mass and size of the VBC. Accelerated release of the VBC may be achieved by the incorporation of inert volatile carriers.40 Such VBC sol-gel coatings are intended for food packaging.

The increase in public awareness of the need for contact disinfection has been stimulated by recent outbreaks of diseases such as SARS (severe acute respiratory syndrome), MRSA (methicillin resistant Staphylococcus aureus) and E coli. Sustained disinfection can be achieved by using a controlled delivery of a highly water-soluble biocide such as poly (hexamethylene biguanide) hydrochloride (PHMB).[41]

Comb copolymers (ie a copolymer that has a polymer backbone with grafted

pendant side chains) can be utilised to prevent bacteria adhering to various substrates.[42] Research has demonstrated that comb copolymer technology allows stable solutions to be achieved when negative charges on the backbone are in the presence of cationic species such as quaternary ammonium compounds or PHMB. Some 70 different comb copolymers were prepared by Gerrard, Annable and Moore based upon four comb copolymer types,[43] namely:

● anionic (ie containing acid-functional acrylic monomers);
● basic (ie containing amino-functional acrylic monomers);
● non-ionic (ie containing non-ionic functional acrylic monomers); and
● amphoteric (ie containing both acid- and amino-functional acrylic monomers).

Formulations prepared from a range of comb copolymers were subjected to a test protocol developed in-house and based upon JIS Z 2801 (2000) in order to allow better prediction of compositions that give both an immediate kill and a sustained surface disinfecting effect.

It was found possible to obtain both an immediate and a sustained biocidal effect using all four types of comb copolymers studied.[43] The key factors necessary for maintaining a sustained biocidal effect through the controlled release of PHMB from a coated formulation were found to be:

● too great a PHMB loading in the formulation leads to a loss of controlled release;
● the molecular weight of the MeOPEG side chain which controls part of the hydrophilic behaviour of the formulation and steric stability;
● the hydrophobic characteristic of the acrylic monomers in the polymer backbone control film solubility and hence the release of the biocide; and
● the charge functionality within the polymer backbone, and how this controls the interactions with PHMB and its subsequent release from a coated film.

Another approach to producing antimicrobial coatings has been described by Tiller et al who prepared reloadable antimicrobial coatings based upon amphiphilic silicone networks.[44] Thus, amphiphilic polymer networks were synthesised, composed of polydimethylsiloxane (PDMS), poly(2-hydroxyethylacrylate) (PHEA) and poly(acrylic acid) (PAA). These were prepared as thin covalently surface-attached coatings via a protecting group strategy.

Atomic force microscopy demonstrated that both the hydrophobic PDMS phase and the hydrophilic PHEA and PAA phase were present at the surface and exhibited nanophase separation.[44] To simulate controlled release, the coatings were loaded with Rhodamine B as a model compound. It was shown that this dye is rapidly released from the pure PHEA-l-PDMS coatings, but from the PAA-l-PDMS coating the release is greatly delayed over several weeks. Preliminary experiments in which the PHEA-l-PDMS coatings were loaded with the disinfectant cetyltrimethylammonium chloride showed that the antimicrobial activity against Staphlococcus aureus was retained after washing.[44] By varying the composition and thickness of the amphiphilic co-network coatings, the amount of antimicrobial or drug loading, as well as the rate of release, could be controlled. Amphiphilic networks appear to be promising for the controlled release of biocides for hygienic coatings in moist and warm areas.

Hygienic surfaces, capable of persistent antimicrobial action against microbial contamination, are now in increasing demand. Williams et al have reported on N-halamine siloxane coatings with a capacity to bind halogens reversibly that have been applied as a 5% solution in a mist or spray, wiped on with a sponge or cloth, or by immersion in a dip bath followed by thermal curing.[45] A wide range of materials were coated, for example polyvinyl chloride, ceramic tiles, paper, cardboard, wood, marble, glass beads, aluminium, stainless steel, a range of organic polymers, grout cement, Formica®, glazed porcelain and silica sand.

After charging with halogen by soaking in 5 or 10% sodium hypochlorite for 30 minutes or by alternative procedures, followed by extensive rinsing in deionised water, the antimicrobial activity was determined.[45] The charged surfaces exhibited potent activity against a wide spectrum of microbes that included yeasts, viruses and fungi. Repeated exposure of charged coated tiles to warm water led to a decline in chlorine levels, but re-exposure to free chlorine resulted in rapid uptake of halogen so that the N-halamine siloxane coating was not removed. Swimming pool liners of polyvinyl chloride coated with N-halamine siloxane in presence of as little as 3ppm halogen might be sufficiently biocidal to prevent the growth of algae and water moulds. These versatile coatings could also be used in incontinence pads/mattress Water-soluble cyclic N-

halamine derivatives such as 1,3-dihalo-5,5-dimethylhydantoin and halogenated isocyanurates have been employed as biocides for industrial and recreational waters for many years.[46] More stable N-halamine compounds for the release of free halogen, such as water-soluble N-chloro or N-bromo-oxazolidinones and imidazolidinones, have also been prepared to increase long-term stabilities in aqueous solution and in dry storage.

Biocidal polyurethane coatings have also been prepared through functionalisation of a reactive diol with a hydantoin moiety which was then copolymerised with commercial polyols and isocyanates to form a polyurethane. Application of a household bleach to provide free halogen then rendered the polyurethane coating biocidal.[47] This work has now been extended by Worley et al to prepare biocidal siloxane coatings.[48] Biocidal quaternary ammonium salt derivatives have been used in the past, but the N-halamine functionality is claimed to provide a much greater biocidal efficacy.

A precursor siloxane monomer based upon 3-triethoxysilylpropyl-5,5-dimethyl-hydantoin was prepared as well as a hydantoinylsiloxane precursor polyme.[48] These were applied by spraying or soaking methods to coat paper and cotton. The treated surfaces were treated with 5 to 10% aqueous solutions of household bleach (sodium hypochlorite) to render them biocidal, and then subjected to bacterial challenge tests using Staphylococcus aureas (ATCC 6538) and/or Escherichia coli 0157: H7 (ATCC 43895). Polyurethane coatings containing the siloxane precursor monomer were also prepared using two different procedures. The results of this study demonstrated that N-halamine siloxane monomers and polymers could be very useful for the preparation of biocidal surface coatings.[48]

Modelling the weathering of coatings

Coatings are designed for control of appearance and for the protection of the underlying surface. However, there is still a major problem in predicting the appearance and protective behaviour of a barrier coating based upon a knowledge of the constituent materials and the ranges of environmental conditions that may be experienced during the lifetime of the coating. While many technologies now rely upon computer design for new product development, coating design, as yet, still relies upon empirical correlations of properties to the coating constituents, then applying and exposing the coating to accelerated testing.[49]

If, however, an accurate modelling system could be developed for coatings, it should prove possible to predict, based on very general and simple assumptions, changes in properties that are functionally consistent with experimental results. Such a theoretical approach potentially could be extremely valuable, and Croll and Hinderliter have demonstrated that change in a coating surface, or bulk, during weathering is the accumulation of repeated, random, nanoscale erosion or chemical events that may be modelled using Monte Carlo modelling techniques.

The temporal changes in the surface topography or chemistry are first modelled using the Monte Carlo approach viewing the evolution of the coating by application of a random process to the surface that removes a portion of the surface. Secondly, various well-known algebraic models or numerical models are then used to predict macroscopic properties such as gloss, fracture toughness, electrical impedance, UV-visible spectroscopy and wetting angle averaged over a spatial region.[49]

Croll and Hinderliter[49] have used the Monte Carlo method together with the Bennett and Porteus model[50] to predict changes in gloss with time of degradation. Similarly, the Griffith crack criterion has been applied using the maximum flaw size generated by the Monte Carlo method to estimate the coating fracture toughness with respect to exposure time.[49] The changes in wetting contact angle have also been simulated using the Wenzel equation for surface roughness. This sophisticated modelling approach has shown that multiphase coatings, including pigments, may be simulated, as well as polymers that change their sensitivity to degradation during weathering.[49] It has been demonstrated that simulated properties change through the lifetime of the coating in ways that are consistent with published results. The Monte Carlo simulations predict trends that qualitatively agree with the published data. In addition, the results obtained scale to appropriate values of service life when reasonable estimates of the UV flux and damage are input.[49]

The extension of the Monte Carlo method, combined with other approaches (eg finite element methods), offers exciting prospects for modelling the random erosion of coating surfaces by photon chain scission, solvent or corrosive species, or mechanical erosion. Clearly the beginning is promising, but much more work is required before the computer design of coatings for new products will become a routine procedure.

Wood coatings

Cost-effective protection for the wood substrate is the foundation for ensuring the successful performance of exterior wood components. While a great variety of decorative effects are available using a wide range of coating types, Miller has pointed out that, in general, service lives remain too short and maintenance requirements are too high for present day circumstances and user expectations.[51]

A key problem is the control of wood moisture content in service, while surface deterioration through photodegradation and weathering and tannin staining are also of concern for high performance in coating systems for joinery. Tannin staining can be decreased through modification in coating formulation, and particularly where 'stain-blocking' pigments are incorporated. End-grain water entry is a problem because the rate of water transmission longitudinally is well-established to be up to two to three orders of magnitude higher than through lateral wood surfaces. The benefits of end-grain sealing of surfaces before component assembly has been shown at the BRE (Building Research Establishment) to stabilise moisture contents during outdoor exposure, and thus enhanced the performance of the coatings.

Other evidence suggests that attention needs to be paid to moisture control on side-grain surfaces because the moisture permeability of many coating systems is too high to prevent excessive moisture content fluctuation in the surface layers of the wood, and hence is detrimental to the long-term performance of the wood/coating combination. Miller asserts that there is a pressing need for a clearer understanding of the relationship between liquid and vapour transmission rates and moisture content of wood in service.[51] In addition, the optimum paint thickness for modern latex paint systems needs to be determined in respect of the protective effect offered. Miller concludes that maintenance paints with a greater degree of 'robustness' need to be designed to improve the tolerance to imperfection of the wood substrate as well as extending maintenance intervals.[51]

Surface finishing of wood with exterior coatings exerts both protective and decorative roles. Stresses set up by moisture can, however, lead to cracking or flaking, while the risk of fungal decay may also occur. The latter may be diminished by pre-treatment of the coated wood with water-repellents, by prior chemical modification of the wood, or by the use of biocide-containing formulations.

Pavlic et al have described the effects of a novel boron-based biocide, an alkanolamine-boric acid ester complex with outstanding solubility in water and ethanol.[52] This exhibits good fungicidal and insecticidal activities as well as fire-retardant activity.[53] The effects of the new biocide on the drying characteristics, stackability, adhesion and permeability of acrylic and alkyd stains on Norway spruce wood was studied.[52]

The drying characteristics of the coatings, or boron-impregnated wood, were most probably altered because of the boron diffusion into coating layers during the drying process. Slower drying led to stickier films. The adhesion to pre-treated wood was not decreased, and in one case was increased. An increase in permeability to liquid water was more evident on the boron-pretreated wood covered with an acrylic coating.[52]

Linseed oil is a renewable natural resource containing high proportions of unsaturated linoleic and linolenic acids, and dries slowly on exposure to air, forming a coating by a complex auto-oxidative cross-linking mechanism that is still not fully understood.[54] It has been widely used in paints, varnishes and in modified alkyd resins.[55]

Stenberg et al have studied the drying of two linseed oils with different fatty acid patterns.[56] Oil A contained 74.2% linoleic acid and Oil B contained 55.2% of linolenic acid. It was shown that the structural variations and the addition of the methyl ester of Oil A (methyl linoleate) as a reactive diluent (at 0, 20 and 40wt%) influenced the drying performance and final film properties of the oils.

The reactive diluent gave softer films but offered the possibility of lowering the use of volatile organic compounds (VOCs). The reactive diluent lowered the viscosity and reacted upon drying with the oils forming a coating on the substrate. For Oil B, which was rich in linolenic acid, the reactive diluent lowered the risk of surface sealing at higher temperatures and the amount of residual unsaturations in the final coating.[56]

The presence of pine wood substrates affected the drying rate for the fat oils.[56] The chemiluminescence results showed a significant shorter induction period for the oxidation reactions when the oils were drying, even without the use of a

drier, when they were applied to wood substrates. These results indicate that further research is needed to establish how different wood substrates affect the oxidative drying process. In this way, the viscosity and chemical reactivity of the linseed oil could be engineered for a particular wood substrate.

Surface treatment of concrete

Concrete may be attacked by many aggressive agencies, among which saline solutions, sulphates, freeze-thaw ionic alterations or carbon dioxide are major agents that can initiate damage both in the concrete or at the reinforcement.[57] Corrosion of the reinforcement can take place if chloride penetrates into the concrete or the carbonation front reaches the reinforcement. Primarily the aggressive agents dissolve in water and are transported into the concrete through the capillary pores. The corrosion processes are considerably dependent upon the moisture content of the concrete.

Hydrophobic treatments of the concrete are applied for protective purposes using silanes, siloxanes, or combinations of both, which penetrate into the pore structure of the concrete.[57] These cover the surfaces without closing the pores or forming a surface film, and react by splitting an alcohol to form a silicone resin, the organic edge groups orienting towards the pore producing a hydrophobic effect. Spray or roller application gives only a limited contact time, but the use of hydrophobic creams or gels, which considerably prolong the contact time, can lead to significantly deeper penetration depth in the concrete.

Raupach and Wolff have conducted extensive research into the efficiency and long-term durability of various hydrophobic agents on different types of concrete using a multi-ring electrode sensor to monitor the variation of humidity of the concrete at different depths by measurement of the electrolytic resistance.[57] It was shown that a more effective hydrophobic treatment was obtained at a dosage level of 200gm^{-2} compared with that achieved at 100gm^{-2}. Concrete samples treated with a product with a high active ingredient content were more effective. Such treatments and solvent-based systems exhibited a greater penetration depth, especially in concrete with a high moisture content. However, there was no conclusive relationship between the penetration depth and the durability of the various hydrophobic treatments. Fur-

ther research is clearly required in order to understand the mechanisms of failure of hydrophobic treatments.

An important aspect of barrier treatments applied to the surface of concrete is the resistance to ion diffusion which ultimately could cause corrosion. Syropoulou and Buenfeld have investigated the characterisation of surface treatments on concrete using AC impedance measurements which are rapid and non-destructive.[58] The electrical resistance of a surface-treated layer is generally indicative of its barrier properties, especially its resistance to ion diffusion.

A test cell geometry that can be used on site has been developed to enable the electrical resistance of a surface treatment to be determined separately from the underlying concrete without the need to physically separate these two elements.[58] Tests were conducted on three different surface coatings, namely, a silane, a polyurethane coating, and an epoxy resin.

AC impedance measurements were found to be successful in assessing the electrical properties of surface treatments on concrete, rapidly and non-destructively, and to also characterise the underlying concrete. A more complicated test geometry was devised for in situ applications, but it was not yet possible to determine the electrical resistance per unit area of surface treatment precisely.[58] It was clear from the experimental results that the in situ technique was sensitive to factors such as coating thickness, degradation and moisture content. Thus, in most practical situations, the sensitivity to moisture content will mean that a period of moisture preconditioning will be required prior to testing.

Metal corrosion

Metals under marine and industrial atmospheres usually suffer serious corrosion because of large amounts of deposited salt and industrial dust particles on the metal surface. However, none of the electrochemical models of salt particles causing atmospheric corrosion could be validated until recently because the corrosion potential could not be mapped with precision. Wang and Wang have recently used a scanning Kelvin probe as a new technique to produce an electrical potential map over a metal surface with a salt particle deposition.[59]

Experiments were carried out on pure zinc and on 20# low carbon steel, polished successively with emery paper and

diamond paste, and cleaned with deionised water and acetone. NaCl, Na_2SO_4 and KCl were ground in a mortar and dried in a decompression tank. Salt particles of 50 to 100μm diameter were used for the study. It was observed that as the relative humidity increased to a level higher than that over the saturated solution of the salt, the electrical potential map changed from homogeneity into heterogeneity.[59] Thus, the electrical potential map changed from flat to a valley initially and thence to a volcano shape. Atmospheric corrosion was initiated by the heterogeneity of the potential distribution because of the formation of anodes and cathodes on the metal surface.

Ambient relative humidity and dry-and-wet cycles were shown to play an important role in accelerating the process of corrosion, as evidenced by the changing potential map which had a close relationship with the chemical maps of the corrosion products.[59] For example, for a NaCl particle on a zinc plate, the valley area was covered with $ZnCl_2$ and the peak area had deposits of ZnO, $Zn(OH)_2$, $ZnCO_3$ and Na_2CO_3.

A model was proposed in which, when the relative humidity (RH) was lower than RH_{OSS} (the relative humidity over saturated salt solution), the whole surface is equipotential, and its map is flat and homogeneous because no electrolyte layer has formed on the metal surface.[59] Where $RH > RH_{OSS}$ the salt particle starts to hydrolyse, forming a thin water layer in which the NaCl dissolves and a corrosion battery is caused by the differential oxygen supply under the water film. Metal dissolution in the central area leads to a potential valley. As the electrolyte layer spreads into the area outside the salt particle, oxygen from the air is dissolved and reduced to OH$^-$ ions. This increases the local pH value and passivates the metal surface. Then it reacts with Zn^{2+} to progressively form ZnO, $Zn(OH)_2$ and $ZnCO_3$ in the presence of carbon dioxide. The deposition of these products on the surface cause the local potential to move positively, leading to a peak in the electrical potential causing the volcano-type potential map.[59]

Pigments

A number of azo compounds bearing phenylazo-2-naphthol structures are used in the manufacture of printing inks. A simple prototype compound of this class, namely, 4'-chloro-phenylazo-2-naphthol (CPAN), was selected by Oktav and Ulgen to determine its printability,

chromatographic behaviour and spectrophotometric colour values.[60] Preliminary results indicated that CPAN could be used as a pigment in offset and oil-based ink production.

CPAN and its potential reduction product, 4-chloroaniline, were separated by a reverse phase high-pressure liquid chromatography system. The pigment CPAN was then incubated at 37°C for 30 minutes at different pH values with nicotinamide adenine dinucleotide (NADH), an important co-factor for the metabolism of organic compounds, in order to investigate whether reduction to the primary amines (4-chloro-aniline and 2-amino-1-naphthol) could occur. However, no such reduction was observed so that the potential toxicity from aromatic primary amines does not appear to be a problem with CAPN.[60]

Film formation in pigmented polymer coatings

The formation of pigmented polymer coatings is complex, and for water-borne polymer dispersed materials depends upon the coalescence of polymer particles as water evaporation occurs. Film formation is thus dependent upon the processes of association, flocculation and coagulation of particles within the pigmented polymer matrix.[61] The effects of light refraction, light absorption, light scattering and light reflection are known to alter the optical properties of a coating and have been discussed by Fresnel,[62] Kubelka and Munk,[63] and Gurevic.[64] The main influence on the optical properties of a coating are considered to be the optical properties of the pigments, fillers and polymers, the composition of materials, and the pigment-polymer and pigment-pigment interactions. In addition, changes in the relief features of the coating surface occur during coating formation.

Film formation of water-borne polymer dispersed materials is accompanied by the weight loss of the coating due to water evaporation.[61] The first, and most intensive, stage occurs because of water evaporation from the surface leaving the coating 'dry to touch', usually with less than 40 to 30% of water remaining in the polymer matrix. As the polymer particles move into closer contact with some deformation of the particles, the rate of water evaporation decreases in the second stage, until in the third and final stage a solid, continuous, filled polymer film is formed and the coating acquires its final mechanical strength.

Zvonkina and Guthrie have determined the colour alterations that occur on 'cold' drying at 20°C by measuring both the reflectance [lightness (CIE L*), chroma (CIE c*), total colour difference (dE*(a,b)) and hue angle (h°)], and the weight loss values over 120 minutes.[61] The reported colour parameters were obtained for the D65 illuminant and 10°-observer functions from the reflectance spectral data. Polymer coatings pigmented with carbon black, phthalocyanine blue, a yellow organic azo pigment and red oxide were studied.[61] The first period of water evaporation led to the greatest rate of colour change. The lightness decreased and the chroma increased, especially with the chromatic, lower-density carbon black, phthalocyanine blue and yellow organic azo pigments, which migrate closer to the coating surface as the water evaporates. Pigment particle migration was also influenced by pigment-pigment and pigment-polymer interaction.

The second period of colour alterations is a transition stage in which the rate of colour change decreases and the different pigments exhibit individual trends.[61] In the final stage the chroma value generally decreases slowly accompanied by a slight growth in the lightness. The former was not observed for the relatively high light scattering power exhibited by the yellow organic azo pigment. This research provides information that could be helpful in enhancing our ability to predict colour features, after coating has taken place, from the liquid state of the coating, and to consider the processes that occur during coating formation.

Modelling fluid flow in printing

In industrial printing processes, liquids are transferred from one substrate to another in order to create a liquid pattern, namely, the wet print. This can be carried out from engraved cavities (eg gravure and pad printing), or by screen printing. However, in contrast to published research on the drop formation from an orifice, which is essential for an understanding of ink jet printing, little experimental or computational work has been applied to explain the liquor transfer in pad or screen printing.[65] For inkjet printing, two numerical approaches that have been adopted to simulate drop formation are a 'volume-of-fluid' method and a Eulerian finite element method.[66,67]

Powell, Savage and Guthrie have reported on two numerical approaches, firstly to simulate micro-scale liquid printing from a trapezoidal cavity to a moving

substrate, and secondly, to model a 'pin-tool' in which a rod is used to deposit a small dot of liquid onto a substrate.[65] The latter are widely used in applications ranging from the spotting of biochips in DNA arrays to the colouring of contact lenses. The authors argue that as industrial competition places increasingly stringent demands on print quality and operation speed, fundamental research into the underlying fluid mechanics of liquid printing is essential, because computational approaches may obviate the necessity for empirical and exhaustive experimentation.[65]

The Lagrangian finite element method enables the fluid flow to consist of fluid particles which are given labels so that natural tracking of moving free surfaces by the connected mesh is possible and moving solid boundaries/obstacles present no special problems. Further details of the Lagrangian methodology and the specific algorithm used have been published.[68] This computational approach is very accurate provided that a suitable mesh can be generated. However, if the free surface deformation is very complex and involves liquid rupture, then the creation of a suitably robust computational mesh can become extremely difficult. Alternatively, a fully automatic mesh generation scheme may be devised, a difficult computational task, or the Eulerian volume of fluid method can be employed.[65]

In the VOF (volume of fluid) approach, a function F is defined whose value is unity at any point occupied by fluid, and zero otherwise.[65] A domain can then be discretised into fixed computational cells, the average value of F in a cell representing the fractional volume of the cell occupied by fluid. A cell with an F value between zero and one contains a free surface. Regions of fluid are tracked through a fixed (Eulerian) mesh rather than the mesh deforming to track the fluid, as in the Lagrangian method. Thus all meshing and logic problems associated with the interface breakup are removed. This enables complicated free boundary configurations to be simulated. However, the VOF method does not exhibit a very high degree of accuracy on small scales because of the use of a fixed mesh. In addition, the authors assert that there is no obvious way of incorporating moving rigid boundaries and obstacles into the algorithm.[65] The recently developed 'frictional area volume obstacle representation' (FAVOR) algorithms may, however, yield a possible solution to this problem.[69]

Powell, Savage and Guthrie have applied the Lagrangian finite element

algorithm to simulate printing a liquid from a trapezoidal cavity, and the VOF method to simulate printing with a pin-tool.[65] Computational approaches to practical cases such as the effect of imperfect cell filling in gravure printing and problems generated by gravity and rotation-driven instabilities are also discussed in detail. Extension of this work to encompass the development of fully three-dimensional codes and incorporation of non-Newtonian rheology is in hand in order to model more realistically the wide variety of liquids (inks) used in printing processes.

Dot gain in printing

Dot gain is a term used to describe the enlargement of features in a printed image with respect to the original to be reproduced. Reduction of dot gain in half-tone printing is desirable in order to reproduce designs accurately in printed format.[70] The spreading of the ink on the substrate after image formation can occur prior to immobilisation by curing or drying, and this is an important contribution to dot gain. Dot gain impairs perceived print quality in the decoration of packaging but can be crucial in more demanding applications (eg the printing of electronic components and circuits).

Bradley and Manning have modelled the spreading of micro-litre drops of a typical UV-curing screen ink (Uvispeed K) on four representative polymer substrates, namely, polycarbonate, polymethylmethacrylate (PMMA), pure poly(ethylene terephthalate) (PET), and surface-coated PET.[70] A modification of the approach by de Ruijter was used to model the spreading of spherical drops of a typical UV-curing screen ink.[71] The drops are considered to be driven towards their equilibrium geometry by a spreading force caused by surface tension effects. The spreading force is dissipated by the effects of the viscous resistance to flow within the drop together with molecular adhesion at the three-phase line (ie solid, liquid and vapour phases). Thus the rate of spreading is determined by this dissipation.

Three parameters have been utilised in the model to describe the rate of spreading,[70] namely:

- the equilibrium contact angle determines the magnitude of the spreading force;
- the friction coefficient ζ_0 arises from molecular adhesion at the three-phase line; and
- the radius, a, of a cylinder within which radial flow can be neglected, describes the flow pattern of the

fluid within the drop, and hence the effect of the viscous resistance to flow.

Thus, measurements of ink surface tension and calculation of the surface energy of the polymer substrates were carried out by the method of van Oss, Chaudhury and Good, and applied to the observed equilibrium contact angles with diiodomethane, water and methyl amide.[72] After the contact-angle and bulk viscosity measurements, modelling and error estimation were carried out.

It was concluded that increasing the ink viscosity can be used to reduce the dot gain, but this approach was restricted because of the operational range of print viscosity required for a given printing process.[70] Ink-substrate interactions could persist for several seconds and were expected to play an important role in determining dot spreading for non-porous substrates with large friction coefficients. The results on pure and coated PET clearly demonstrated that by strengthening molecular adsorption, it was possible to increase friction at the three-phase line without a decrease in the equilibrium contact angle.

The ideal polymer for minimising the rate of drop spreading would contain polar groups with large partial charges within the dipole, with the dipole centres physically and electronically well separated by non-polar aliphatic or aromatic linkages.[70] This would maintain a surface, primarily hydrocarbon in nature, without significantly altering the surface energy. The wetting characteristics would thus remain similar, but slower-spreading dynamics should contribute to image reproduction and stability without creating potential problems of de-wetting in solid image areas.

In gravure printing, the changes in colour strength are achieved principally by the use of half-tones, a matrix area of dots of varying area coverage. During printing some factors affect the size of the half-tone dots, a feature termed dot gain. Gencoglu has investigated the effects of polyester, BOPP (bi-axially oriented polypropylene) co-extruded and BOPP plain films as printing substrates, as well as the engraving parameters on solid density and dot gain in gravure printing.[73] BOPP is used in numerous industries, for example food packaging, printing/laminating and labelling.

The surface properties of the films were characterised by measurements of surface tension and water contact angle, while the surface roughness was determined using atomic force microscopy. A solvent-based black commercial gravure

ink (based upon a nitrocellulose ester binder) was used in a proof printing machine, printing a gradation scale which was engraved four times using a Hell Klishograph unit with four different parameters. Print evaluation was carried out by measuring the solid density and dot gain using a Gretag Macbeth D19C portable reflection densitometer which was calibrated by a calibration card before the measurements.[73]

From this experimental study, it was concluded that where the film surface roughness increased, so did the solid density. Engraving deeper and fewer cells per cm^2 yielded lower solid density values compared with shallower and more cells per cm^2. Interestingly, the surface tension of the print substrate exerted no effect upon the solid density value obtained.

It was shown that engraving parameters did have a major effect on the dot gain, the highest dot gain being observed on the smoothest substrate, polyester. The highest dot gain values were also observed on the 35% half-tone area of all the scales printed on the substrates.[73]

When cells with channel and without channel were compared at the 35% half-tone area, the dot gain increased in cells, with a channel having fewer cells per cm^2 and a greater depth.[73] Dot gain decreased in the cells with no channel. Channels between cells had an effect on dot gain. Cells with more channels and more cells per cm^2 demonstrated greater dot gain in the highlight area (3 to 10% coverage), whereas cells without channels and fewer cells per cm^2 showed more dot gain for all the substrates in the 10 to 50% coverage zone, termed the mid-tone area.

Inkjet printing

Inkjet printing has many advantages over conventional screen printing, but comparisons of textile print quality are essential if this new technology is to expand its influence industrially. A comparison has recently been carried out by Kiatkamjornwong et al.[74] An acrylic binder, S-711, was used with a pigment-to-binder ratio of 1:2 (by weight) for one set of inks; BR 700 was used for another set of inks. The ink viscosity was increased to meet the rheological requirements by adding fume silica. The ink viscosity and particle-size distribution both increased slightly during storage at ambient temperature for two months.

For inkjet printing, cotton fabric was washed, dried, ironed and pretreated

with poly(ethylene oxide) (2 to 3 million Dalton molecular weight). The printed fabrics were analysed for colour saturation and colour gamut, and their volume, density, tone reproduction, stiffness, air permeability and crock (rub) fastness determined by standard methods.[74]

The print quality of the inkjet printed cotton fabric obtained by multi-pass printing, as determined by colour gamut, volume, stiffness, air permeability and crock fastness, was superior. However, even though the loaded ink volume was tuned to be the same as that given by the screen ink, both printed fabrics gave different colour saturation, colour gamuts and tone reproduction.[74]

The inkjet printed cotton fabric had to be printed three times to produce the same colour and tone reproduction as that produced by screen printing, indicating some of the current limitations of inkjet printing for industrial textile printing.

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