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# RadTech Barcelona

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## A review of the lectures and exhibition (18-20 October 2005)

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#### Pictures from an exhibition

The Convention Centre used to host the conference and exhibition provided excellent facilities for the 600+ delegates who attended and the 40 companies who exhibited their products.

The exhibition was accommodated in a large room which afforded plenty of space for the exhibits and for delegates to network. Exhibitors included the major resin producers such as Cytec, Rahn, Sartomer, BASF, Bayer, Synthesia Espanola, Daelim from Korea, AGI Corporation Taiwan and Schenectady International.

Schenectady have an interesting range of resins for the electronics industry and are also acting as agents for the Ashland Corporation with their new range of resins derived from acrylates via the Michael addition of compounds containing active methylene groups (see later for examples).

Photoinitiator supply companies were well represented by the presence of Ciba Specialty Chemicals, Lambson Fine Chemicals, Lamberti, IGM Resins and New Sun Corporation, with much interest being shown in new cationic photoinitiators and alternatives to isopropyl thioxanthone.

There is still much interest in nanoparticles with Clariant and Hanse Chemie AG showing their range of nanoparticulate materials. Producers of additives were represented by Byk-Chemie, Degussa, Kromachem, NPS – Novel Polymer Solutions, Tego and Noveon Special Additives.

Major producers of lamps were present (Fusion Systems, Dr Honle, IST Metz, Jenton International, Nordson UV, Phoseon Technology, UV Process Supply and UV-Tec Messtechnik, Hamamatsu Photonics) with much interest being shown in the use of LED lamps for curing.

Solatell and Jenton International showed equipment for monitoring lamp performance. Ushio Europe kept the flag flying for electron beam equipment with emphasis on low voltage systems. Linde showed how generating gaseous nitrogen by nitrogen take-off can be integrated with water cooling of lamps and reflectors thereby reducing the cost of nitrogen inerting.

The growth areas in the inks market were represented by Mirage inks (cationic inks) and Xenxia Technology (ink jet). Chemidex was demonstrating its

extremely useful database of companies and their coatings products, which can be an invaluable aid when tracing suppliers of desired materials.

#### Matters of protocol

The opening lectures were concerned with how to expand and promote the use of radiation curing and in particular how to address negative perceptions of the technology. There was a feeling of frustration that there hadn't been a greater utilisation of our 'Green' technology.

In the review which follows, papers are identified as being published in Part I or II of the proceedings and by their page numbers.

To allay the fears of would-be users, RadTech Europe has produced a UV Protocol (to aid the safer use of radiation curing in the coating and printing industry) which was adopted at the conference (M Riestler, B Kuter, A Meyer, I, p 25).

The fastest growing economy for radiation curing is Asia, and it is anticipated that the Asian, European and North American markets will be of similar size by 2015. It is expected that use of radiation curing in the automotive industry will be growing by 2008. There must be further growth potential based on the fact that coatings can now be applied to substrates ranging from metals through plastics to natural polymers such as leather and from the fact that tough, flexible and elastic coatings can be produced (based on urethane chemistry).

Much work has been done to expand the use of radiation curing for 3-D objects, both by lamp manufacturers and formulators (eg through dual cure systems) and curing of pigmented systems can be successfully carried out.

#### Parallel processing

Following the introductory session, three sessions were run in parallel with sessions on wood coatings, automotive coatings and equipment taking place on the first afternoon. In the Equipment section two lectures were given on low voltage EB units. Some very small laboratory units are available which use sealed tubes as the source of an electron beam (Ushio Europe). The price of the successful low voltage wide web curing units from Energy Sciences is being reduced, which will make the use of EB more competitive with UV curing.

An excellent lecture was given on dosimetry which showed how laboratory results could be transcribed with confidence into production (I Rangwalla, I, p 115). For UV curing units, innovative and practical ways of heat management were shown (O Treichel, I, p 123) and a simple way of converting the conventional UV dryer into one that allowed nitrogen inerting (G Rames-Langlade, I, p 133 and P Cocolios, I, p 447).

In this and other lectures, the benefits of nitrogen inerting were emphasised - eg full cure can be attained with either lower concentrations of PIs (lower odour of the cured coating and fewer migratables within the coating) or reduced lamp power (which aids curing films applied to heat sensitive substrates) and better surface cure.

Use of LEDs operating at 395 nm is generating interest. The intensity of the emitted light of these devices can be increased by running with a high current, but if the intensity is to be maintained it is necessary to water-cool the power generating unit of the LED (R Little, I, p 139).

It is clear that with the current technology, use of LEDs is restricted to narrow web or 'spot-cure' type applications since the cost of making up a vast array of LEDs is prohibitively expensive. An excellent appraisal of the advantages and disadvantages of using LEDs was presented (P Mills, I, p 157).

A fascinating lecture on the potential use of UV plasma curing for producing coatings for the auto industry was presented (T Jung, I, p 169). The technique of plasma curing was explained and then it was shown how plasma could be used to cure coatings applied to automobiles. The urethane acrylate formulation containing photoinitiators is applied, the vehicle is put in a chamber which is evacuated and then the plasma ignited or using the words of Dr Jung, 'the coating is cured within the lamp'. Coatings produced in this way are hard and durable and show no extra yellowing. There is every indication that there is a serious intention of commercialising this process.

## Woodcoatings update

Two sessions were devoted to aspects of wood coating. The problems associated with microwave drying of waterborne coatings were summarised (C Swaboda, I, p 33). It was shown that waterborne polyurethane dispersions can be used to produce high performance coatings suitable for kitchen and bathroom applications (D Mestach, D R Twene, II, p 219).

An appraisal was given of the current position of the application of powder coatings to MDF with the conclusion that the process is still in its infancy but showing promise for the future (S Santandrea, I, p 43). In a later session, the question as to the storage stability of powder coating formulations was addressed with the emphasis being on the use of mixtures of crystalline and amorphous resins (E Spyrou, II, P 267).

A new approach to inerting with carbon dioxide was described in which 3-D objects were passed through a tank filled with the gas. Since the density of carbon

dioxide is 1.5 times that of air, the gas sits in the tank and hence the need for gas replenishment is minimal (M Biehler, E Beck, K Menzel, S Titusson, A Daiss, K Soljamo, K Fagerholm, I, p 57).

Some excellent results have been obtained by printing (using indirect gravure printing) directly onto wood, which raises the question as to the future of furniture foils (J Voigt, I, p 67).

Coatings for laminate floors, which is undoubtedly a major growth area, received attention (A Vahlhaus, I, p 79) with the use of nanoparticulate silica (F Bauer, R Flyunt, K Czihal, H Glasel E Hartmann, R Mehnert, I, p 407) and alumina (J Hajas, P Lenz, and K Schulte, I, p 415) being advocated for improving scratch and abrasion resistance and methods for testing these coatings were described (K Bisbruck and J Prieto, M Poitoux, I, p 397). Lectures relating to furniture coatings dealt with such aspects as legislation (R Nussbaum, I, p 53), ways of developing a matt finish (C Tunice, I, p 381, M Sudder, I, p 389) and the merits of using polyurethane dispersions (C Irle, M Bayona, I, p 371).

## Automotively speaking

There was a session on coatings for the automotive industry. Polyurethane dispersions based on epoxy acrylates have been shown to have excellent adhesion to metals, but an innovative approach to polyurethane design has produced relatively low viscosity materials facilitating spray application of formulations.

These new materials contain allophanate groups (produced by reacting a urethane with an isocyanate) which prefer to form intramolecular rather than intermolecular hydrogen bonds and hence possess lower viscosities than the conventional urethanes (W Fischer, H Kuczewski, D Rappen, J Wekard, I, p 185). The chemistry behind these materials and their method of manufacture was further developed in the 'New Chemistries' session, (M Ludewig, N Stockel, J Wekard, I, p 261). Other formulations (solvent-free and applied by roller coating or spray coating) based on conventional polyurethanes and containing nanoparticulate silica have been explored (J Amigo, M Arranz, G Frezel, I, p 193) and shown to give good durable coatings.

An excellent clear-coat system for the auto-refinish market has been devised which is based on the reaction between thiols and isocyanates. Photoinitiation is by generation of a base with the initiators (activated by UV-A light) belonging to the class of  $\alpha$ -aminoacetophenones (N Dogan, H Klinkenberg, L Reinerie, D Ruigrok, P Wijnands, K Dietliker, K Misteli, T Jung, K Studer, K Contich, J Benkhoff, E Sitzmann, I, p 201).

Presumably the amino group in the acetophenone is weakly basic (due to inductive and steric effects) but following  $\alpha$ -cleavage the generated amine is a much stronger base due to removal of the inductive effect of the carbonyl group and a reduction in steric hindrance.

Two-pack formulations which may be spray coated are used (the reactive components in one pack and the

latent base – PI in the other). Curing of auto refinishes has also been brought about by the use of flash lamps (J P Stropp, U Wolff, W Schlesing, S Kernaghan, H Löffler, M Osterhold, H Thomas, I, p 215). The curing of 3-D auto parts requires careful design of the lamp system and some such systems (including robotic systems) were described (K H Joesel, p221, O Starzmann, I, p 229).

## New chemistries described

In the session on 'New Chemistries', the attractive non-isocyanate route to urethanes (based on cyclic carbonate chemistry) was described (J van Holen, V Stone, H Van den Bergen, I, p 235). The synthesis of oligomeric acrylates with built-in photoinitiators using the Michael addition of  $\beta$ -dicarbonyl compounds to acrylated reactive diluents was described and their applicability to wood coatings, inks, electronics outlined (M L Gould, S Narayan-Sarathay, T E Hammond, R B Fechter, I, p 243). An attractive feature of the use of these materials in inks is the low levels of extractables in the cured coatings.

Metal-containing (meth)acrylates such as zinc dimethacrylate have been known for some time and now ways have been found to make such materials more compatible with conventional acrylate resins and diluents (G Ceska, C Leroy, B Schaeffer, I, p 253). The ionic crosslinks generated by these materials lend valuable properties to the cured coating, such as self-healing.

A new cationic photoinitiator (based on thianthrene and now commercialised) was described and its performance in various inks given (M Visconti, E Casiraghi, E Bellotti, I, p 269). The initiator has the virtue of neither generating odorous byproducts nor benzene.

The old chestnut of increasing matting by incorporation of silicas was addressed, where it was stated that matting is not generated by silica particles floating to the surface of the film during cure and the observation was made that the more thixotropic a coating the better the matting (H-D Christian, I, p 279).

Thiol-ene chemistry surfaced in the form of the use of ene-substituted oligomeric silsequioxane (POSS) particles as reaction partners (C Hoyle, T Clark T Y Lee, T Roper, B Pan, H Wei, H Zhou, J Lichtenham, I, p 287). The POSS particles can be used to increase the hardness of coatings and to reduce their flammability.

Urethane acrylates containing allophanate groups and isocyanate groups have been synthesised and used in dual cure formulations (Y Heischkel, R Schwalm, M Kutschera, W Schrof, S Kolzenburg, E Beck, H Larbig, K Menzel, N Gruber, I, p 295). Polyols are incorporated into the formulations so as to introduce further crosslinks following irradiation and hence increase the hardness of coatings and as a means of getting cure in shadow areas.

In the session entitled 'Printing, Varnishing and Laminating for the Packaging industry' all seven papers were concerned with the use of EB processors and assessing the virtues of this technology. A particular virtue of value to the food packaging industry is the lack

of PIs, and since cure is carried out in a nitrogen atmosphere an amine synergist is also unnecessary.

In an attempt to improve the efficiency of amine synergists, a polyglycol bis-dimethylaminobenzoate has been synthesised (D G Anderson, C A Bell, R S Davidson and P Sellars, I, p 435). The liquid product proved easy to formulate, was effectively incorporated into the cured coating although its effectiveness at combating oxygen inhibition in thin films was not as high as expected.

The use of a low-cost nitrogen inerting system to aid plasma chemical grafting of nitrogenous compounds onto the surface of polymers has been explored and appears to offer a way of increasing the adhesive properties of polymer surfaces (P Cocolios, I, p 445). Further improved wetting and dispersing agents for use with radiation curable formulations (particularly flexo inks) were described (P Cavaleiro, P Lange, S Oestreich, I, p 453).

The performance of a new polymeric benzophenone and thioxanthone PI in some inks was outlined, and whilst use of these materials may lead to slightly lower speeds of cure they offer advantages such as lower odour and extractables within the cured film (F Bertens, Y Qingjin, D Gu I, p 471).

A particularly innovative development is that of UV-curable toner powders which can be applied to substrates using conventional electrophotography thereby offering an alternative to inkjet technology (L Deprez, W Op de Beeck, I, p 479).

The successful coating of plastics with radical curing formulations presents difficulties, but new materials which swell the plastic and have a surface tension lower than the substrate have been developed and can be used to overcome adhesion problems (S Smeets, I, p 501).

Some new semi-crystalline polyurethane resins have been developed for the powder coating market and are particularly useful for coating heat-sensitive substrates (F Williams, J Armengol, E Grau, C Chambat, C Laurens, I, p 531).

Nanoparticulate silica has been utilised in topcoat formulations to protect both hard and soft basecoats, and leads to improved scratch resistance and improved hardness (C Vu, O La Ferte, A Eranian, I, p 541).

The use of hyperbranched polyols in cationic curing formulations to coat polyolefins has been shown to improve the rheological properties and speed of cure of the formulations (D James, p Appelkvist, E Gustavsson, I, p 551). In the area of adhesives, the use of copolymerisable photoinitiators in pressure sensitive adhesive formulations has been explored with acrylated 4-hydroxybenzophenone being the best performer (R Milker, Z Czech, I, p 571).

Evidence supporting the view that cationic curing systems offer advantages over radical curing systems for the production of silicone release coatings was put forward (S Herrwerth, I, p 581).

The influence of temperature on the cure of epoxides and acrylates has been investigated, and not surprisingly it

was found that an increase in temperature benefited both systems (A Hartwig, M Popp, K Teczyk, I, p 609). Increasing humidity increased the rate of consumption of epoxide groups, but since this is a reflection of increased chain transfer, it is likely that film properties decreased with increase of humidity.

Acrylation of glycidyl versatate gives a product which may be used as reactive diluent and appears to improve adhesion on polypropylene (A Fronze, H Hendrickx, N Henry, D Heymans, I, p 615).

A useful twist on the well-known thiol-ene reaction was the inclusion in the formulation of a species that could undergo addition-fragmentation chain transfer reactions (C Bowman, II, p 7). Irradiation of the cured films relieved stress in the films and enabled the thiol-ene reaction to be used to generate shape-memory coatings (for full details see – T F Scott, A D Schneider, W D Cook, C N Bowman, Science, 2005, 308, pp 1615-1617).

Further evidence was presented that supports the view that pre-organisation of acrylate monomers through hydrogen bonding increases the rate of cure (S Jonson, T Y Lee, T M Roper, C E Hoyle, C A Guymon, II, p 23).

The extent to which hydrogen bonding plays a part in real formulations will be determined by the hydrogen bonding characteristics of other components.

The use of oxetanes in cationic curing formulations is far from new, but now a new range of compounds, including hyperbranched species, containing oxetanyl groups has been prepared (T Nishikubo, A Kameyama, II, p 41). In a series of cleverly designed experiments it was shown that increasing the viscosity of a formulation does not always lead to retardation of cure (E Andrzejewski, M Janaszczyk, M Andrzejewski, II, p 49).

A rather specialised area of radiation curing is two-photon induced polymerisation, which can be used to fabricate microparts (K Belfield, S M Kuebler, C Yanez, II, p 75). For two-photon polymerisation to occur it is necessary for the laser beam to be tightly focused and for the photoinitiators to have special absorption characteristics.

An innovation for the conference was the inclusion of a session on Health and Safety (seven papers) which fitted in well with the launch of the new protocol and the impending implementation of REACH (Registration, Evaluation, and Authorisation of Chemicals). It is clear that unless a sensible protocol for implementation of REACH is found, the chemical industry, of which the surface coatings industry is only a part, could suffer dire consequences. The value of having well-informed lobbyists cannot be underestimated. It is probably going to be true that over the next few years the only new materials to be introduced to the market will be those designed with legislative restrictions in mind rather than designed for optimal performance.

Under the heading 'Innovations' a fascinating lecture was given on rapid prototyping in which the 3-D models are built up using an inkjet printer (E Napadensky, II, p 191). The raw materials are contained in a cartridge so that the operator has no need to come into direct contact

with them and the whole unit is designed so that it may be used in an office environment.

Despite the polymerisation system being based on acrylate chemistry it was claimed that little shrinkage occurred on cure and that there was no need for nitrogen inerting.

A very interesting paper on the application of hyperbranched resins, which offer advantages such as high reactivity, good pigment wetting and relatively low viscosity, teased the audience and in some cases thoroughly disappointed them, by giving no indication as to the structure of the materials or the chemistry lying behind them (J M Oliver, M Bernard, H Cavalié, II, p 199).

## Photochemistry sessions

In the photochemistry section, further attention was paid to hyperbranched polyesters which in this case were modified by attaching phenolic residues (M Sangermano, A Di Gianni, R Bongiovanni, A Priola, B Voit, II, p 239). These additives decrease the T<sub>g</sub> but unusually increase the impact resistance and modulus of the coating.

In one of two papers devoted to the application of radiation curing to the electronics industry, the design of resists which could be easily removed by chemical treatment following cure (cationic) was described (M Shirai, II, p 249).

Such materials are useful when it is desired to remove failed components from a circuit board. The design of new photoinitiators such as a 'low migration' Type I photoinitiator, bifunctional glyoxalates for non-yellowing, low migration applications, surface active photoinitiators and photolabile bases were described (J Benkhoff, K Dietliker, T Jung, K Powell and E Sitzmann, II, p 297).

There was a very timely paper presented on hybrid sol-gel coatings where it was shown that addition of titanium alkoxides to silica systems leads to enhanced photosensitivity (C Croutxe-Barghorn, M Feuillade, D J Lougnot, II, p 303).

There was a well supported poster session containing 22 papers covering a wide range of topics from spectroscopic investigations of the mechanism of breakdown of photoinitiators, amino acids as amine synergists, through to medical applications (bone replacement materials).

## Conclusions

My overall impression of the conference was very positive, since new chemistries are finding their way into products and application thereby opening up new markets and this despite the potential negative impact of REACH.

It was good to see some new names at the exhibition and the sterling efforts that equipment manufacturers are making to accommodate the needs of different industries. I am therefore looking forward in keen anticipation to the 2007 meeting!

