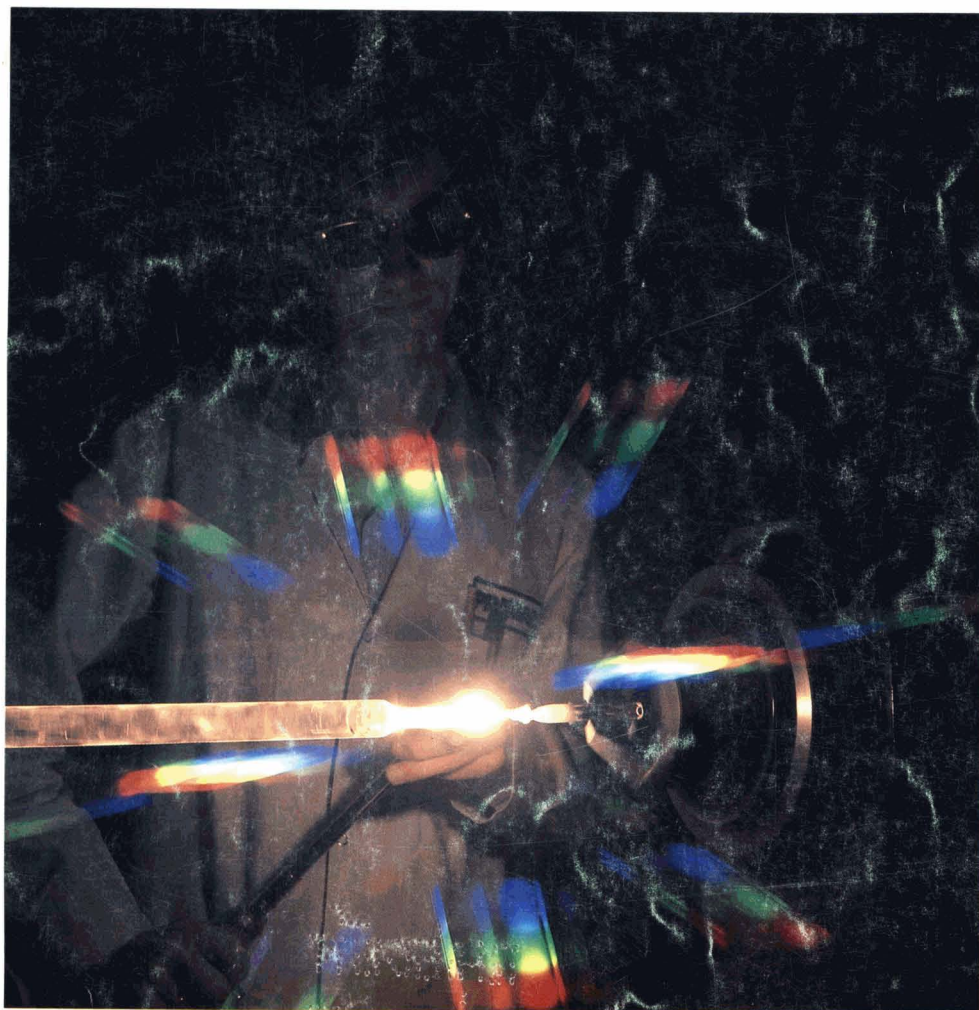JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION

JOCCA

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Contents

Cover: UV lamp manufacture – Quartz lamps of wavelength 254nm used in UV curing. (Photo by courtesy of Primarc Limited, Slough)

Forthcoming Features: December – Weathering; Process Operation (PO), Feeding and Packaging; January – Greener Coatings; PO, Filling & Weighing; February – Polymers & Resins; PO, Small order manufacture.
Contributions are welcomed at least five weeks prior to publication date.

From the Honorary Editor

JOCCA
JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION

EDITORIAL PROGRAMME 1991

The **1991 Editorial Programme** for the Journal has now been approved by Council and is given in full below. The Publication Committee's policy is to attempt to cover items which are of importance and interest to the members of the Industry and thus each year we repeat such items as polymers, solvents and pigments which are vital ingredients to surface coatings and in which many interesting changes take place during the year. New topics are also chosen and we will always be pleased to receive from our readers suggestions for items suitable for inclusion into the Feature Programme.

The high quality of scientific and technological papers, for which the Journal has become well known, will be maintained in the Transactions and Communications of the Journal each month. We will also publish from time to time papers of a more general nature intended to assist the newcomer to the Industry and possibly be of value to the more experienced reader as revision.

The various exhibitions and conferences which are to be held in 1991 will be fully reported. We ask any reader who is in position to submit a suitable paper to contact either the Hon Editor John Taylor or the Assistant Editor Peter Fyne on the following telephone numbers 0443 734893 or Priory House 081 908 1086 or Fax 081 908 1219. We have now installed Desk Top Publishing Equipment at Priory House and accept items on any magnetic media.

Next follows the 1991 Editorial Programme .

J. R. Taylor
Honorary Editor ∎

MONTH	FEATURE	SUPPORTING FEATURE
January	Environmental challenges to the surface coating industries	Filling and weighing
February	Polymers and resins	Small order manufacture
March	Corrosion	Equipment for quality control
April	Pigments	Instrumental colour measurement
May	Powder coatings	Detection and measurements of atmospheric solvent level
June	Additives	Paint and ink manufacturing plant
July	Printing Inks	Environmental problems with waste disposal and recycling
August	Solvents	Curing methods
September	Biocides in the surface coating industries	Finishing '91—Preview
October	Rheology and paint application	European Paint Show—Preview
November	Weathering	Transportation of surface coatings in bulk and in containers
December	Waterborne coatings	Analytical methods

SURCON 91 SURCON 91 SURCON 91

All those who actually read the Journal will know that the next bi-ennial OCCA Conference (now known as SURCON 91) will be held at the Moat House International Hotel at Stratford-upon-Avon from 12-14 June 1991 (with facility for staying on until the Saturday morning).

After the usual considerable thought the cost to delegates has been decided and agreed and will form the basis of the actual registration brochures to be circulated in due course. This time we have attempted to encourage people to book early and so there will be a discount for those who book BEFORE 9 March 1991.

DELEGATES

Members - full registration fee £220
Non-Members - full registration fee £260
Day Registration - Members £120 Non-Members £160
Retired / Student Members £140
Lecturers £140
Bed and Breakfast at conference hotel (special negotiated rates): £61(Single), £87(Double/Twin)

NON-DELEGATES

£15 per day - for those not resident at the conference hotel, covers all trips.
£90 per day - for those resident at the conference hotel, covers all meals and includes the conference dinner and Cotswold Supper (if on the day paid for) and all trips.

SPECIAL ITEMS

For those not covered by the above, the following charges apply:

CONFERENCE DINNER - £33

COTSWOLD SUPPER - £25

It is hoped that all delegates and non delegates will stay in the conference hotel and avail themselves of the favourable rates negotiated by the Conference Committee. Overnight stay in alternative accommodation must be arranged by the individuals concerned - 'Priory House' will be glad however to assist in nominating places for such alternative overnight stay in the area.

Simon Lawrence will report upon the subject and the authors of the papers to be presented, which leaves me to finish things off by giving a brief outline of the Social programme.

12 JUN - a.m. Golf Tournament at Staverton Golf Club, p.m. Overseas Visitors' Reception (buffet by Herald Press), Trip to Memorial Theatre for a Play - Coffee andSandwiches at Hotel.

13 JUN - a.m. Tour of Stratford-upon-Avon, p.m. Visit to Warwick Castle (afternoon), Informal Dinner (evening)

14 JUN - a.m. Day Trip to Blenheim Palace via Broadway and Woodstock - return by 4.15 p.m, p.m. Cotswold Supper Trip

15 JUN - a.m. Depart

I hope that the subject matter of the papers as detailed by Simon Lawrence, appeals strongly and that great support is occasioned to be enhanced by the locale and non-technical programme.

A. C. Jolly - Honorary Conference Officer ■

(A further technical announcement will appear as a loose insert with this issue of JOCCA)

Jenson & Nicholson acquire Cementone-Beaver and Windeck Paints

*J*enson & Nicholson has acquired Cementone-Beaver Ltd, Windeck Paints Ltd and fifty per cent of Buckingham Coatings Ltd for £12.2 million to give it a major paint manufacturing base in the UK. The acquired companies were previously subsidiaries of CH Industrials PLC.

Jenson & Nicholson is one of the largest paint companies overseas, manufacturing some of the most popular brands - Berger, Crown, Robbialac, Brolac, Luxol and Magicote - with interests in Africa, Asia, the Far East and the Caribbean. These acquisitions furthers its strategy to establish Jenson & Nicholson as a major player in the world paint market.

Cementone-Beaver produce a range of decorative paints for decorators/ contractors, building chemicals including cement additives and dressings, Wykamol preservatives, and injection damp-proofing products.

Windeck Paints produce a range of decorative paints, mainly own-label products, for the DIY retail market.

Buckingham Coatings owned 50/50 by Jenson & Nicholson and Sigma Coatings (a subsidiary of Petrofina), manufacture paint for Cementone-Beaver and Sigma Coatings.

Through its association with the huge Indian conglomerate, The UB Group, Jenson & Nicholson will be able to provide Cementone-Beaver and Windeck Paints with substantial

Vijay Mallya, Chairman of Jenson & Nicholson Ltd and The UB Group

resources for expansion - not only in the UK but overseas through Jenson & Nicholson's 24 manufacturing companies. It will also give the companies access to greater purchasing power of raw materials and to advanced paint technology held by the parent company.

Brian Davies, Deputy Chairman of Jenson & Nicholson, commented, "the acquisition of Cementone-Beaver, Windeck Paints and a fifty per cent stake in Buckingham Coatings gives all parties tremendous opportunities for expansion worldwide. Not only will they be able to benefit from our overseas strengths but we will gain valuable experience from them on the UK paint and coatings market."

Mr Davies continued, "everyone involved is very enthusiastic about the deal and as Cementone-Beaver, Windeck Paints and Buckingham Coatings have all performed well over the past year, despite the downturn in the UK economy, we view the future with confidence."

Brian Davies, Deputy Chairman and Managing Director, Paints Division, Jenson & Nicholson Ltd

The acquired companies will be run autonomously and their relationships with suppliers and customers will not be affected.

Gulf crisis likely to push up ink prices

*T*he Society of British Printing Ink Manufacturers forecast that the cost of mineral oils to the printing ink industry is likely to increase dramatically, newspaper inks in particular, with their high mineral oil content, being substantially affected. As a consequence, increases in the prices of printing inks are inevitable because most kinds of inks contain materials of petrochemical origin.

BASF establishes new coatings company in Mexico

*B*ASF's two subsidiary companies in Mexico, Inmont de Mexico and Pinturas Aurolin have joined forces to form a new company, BASF Pinturas + Tintas (BPT). The company will employ around 800 people and will operate within BASF's coatings and inks, and printing systems divisions. Expected operating turnover for the first year will be DM 80 million.

Ellis & Everard buy Hilton Products

*E*llis & Everard plc, the UK's leading independent chemical marketing and distribution group, has reached agreement with ICI to buy its Irish subsidiary, Hilton Products Ltd. Based in Dublin, Hilton Products specialises in the distribution of solvents. Ellis & Everard have already national chemical distribution throughout Ireland from Ellis & Everard in Belfast; Eurochem Ltd in Dublin; and Chemplus Ltd in Limerick.

Eastman diketene capacity up

*E*astman Chemical Company, Kingsport, Tennessee, recently completed a debottlenecking project on Diketene which increased capacity by 20%. This will enable Eastman to increase production of Diketene derivatives to meet growing demand for these intermediates. Diketene derivatives, such as methyl acetoacetate, ethyl acetoacetate, acetoacetanilide, and monomethyl acetoacetamide, are intermediates for the production of pigments.

Dow to produce glycidyl methacrylate

*D*ow Chemical has announced plans to produce glycidyl methacrylate (GMA) at a new manufacturing facility to be constructed in Freeport, Texas, USA.

CIN'S big advance in Portugal

*T*he largest Portuguese-owned paint manufacturer, CIN, has acquired a controlling interest in Portugal's fifth largest paint company, Sotinco S.A from Quimigal S.A., Portugal's largest chemical group. CIN's main factory is located near Oporto in northern Portugal while Sotinco's plant is at Barreiro, south of Lisbon. Both companies have sales offices throughout Portugal .

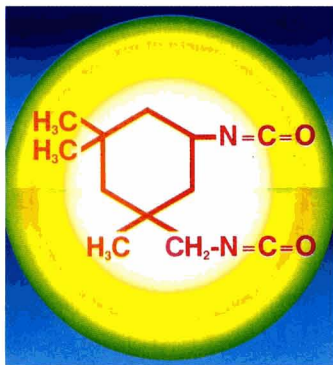CIN Chief Executive Joao M. Serrenho said: "Sales for the CIN

Late News: ICI has purchased from Cookson the other half of Tioxide for £171m.

group in 1990 will now exceed 10 billion escudos (65 million US Dollars) putting it on a par with our strongest competitor in the Portuguese market." The acquisition of Sotinco by CIN conforms with Quimigal's strategy of concentrating on its core business and CIN's programme of expansion in its chosen area of operations. Sotinco's sales in 1990 are estimated at 2.5 billion escudos. The company produces decorative paints, heavy duty and marine coatings, metal and wood finishes and automotive OEM and refinish coatings.

Call for European Paint Club

On the 8 September at the invitation of WGH + Partners AG - a Swiss international consulting company for the paint industry- a small group of proprietors of middle-sized and large paint factories from Holland, Germany, Switzerland and Italy got together in Zermatt. Five lecturers explained to the symposium participants the wide variety of chances for the paint industry offered by European cooperation, as well as the dangers and limitations.

T. H. Kaffenberger

As a result they agreed there was a necessity to build up cooperation between like-minded, small and medium-sized paint factory owners at a European level Dr. T. H. Kaffenberger, the chairman of the symposium, presented the model of a "EUROPAINT CO-OP AG" based and developed on actual practice. It was announced that the cooperation would start off with an information system on the costs of acquiring raw materials.

As the first step in this direction, one of the lecturers, Dr. Willy Simson, called for the founding of PAINT CLUBS. Like-minded paint manufacturers from various countries could meet and exchange thoughts in these paint clubs without a lot of formality. This would be the right soil in which to cultivate the founding of one or more "EUROPAINT CO-OP AGs", said Willy Simson.

Based on this strong response, WGH + Partners AG, P.B. 11 in CH-3912 Termen/VS will hold an international symposium on 18 January 1991 in Geneva, with the aim of conducting the first meeting of a large paint club.

For further information call Switz.028-243200.

Products

New Halox inhibitive pigment

HALOX SZP-391, a new strontium-zinc complex, nontoxic, chromate-free pigment, developed to provide corrosion resistance equivalent to zinc chromate and other chromate pigments in a variety of trade paints and industrial coatings, has been introduced by Halox Pigments. Highly versatile and easy to formulate, the new pigment is compatible with a variety of resins, and proven effective in a wide range of pigment loadings. HALOX SZP-391 is an excellent candidate for use in high solids formulations, powder coatings, and baking systems for heavy duty maintenance, OEM products finishing, and coil coating applications.

For further information Enter K101

Riedel-de Haen algicide

A new grade of Mergal® algicides has been launched by Riedel-de Haen, a member of the Hoechst Group of Companies. The new grade Mergal S90 is a film preservative for external use. A significant benefit of Mergal S90 is its resistance to leaching, giving longer efficacy in the paint film. Additionally, Mergal S90 does not contain halogenated components and cannot contribute to AOX (adsorbable organic halogens). The product therefore reduces the build-up of materials in ground water.

For further information Enter K102

New Mearlin® pearlescent pigments

Mearlin® Inca Gold and Mearlin® Sunset Gold are new, metallic-like gold pearlescent lustre pigments introduced by The Mearl Corporation. Both new pigment

grades consist of iron oxide coated mica, and are applicable for incorporation into most plastics, surface coatings and printing inks. Mearlin Inca Gold has a particle size range of 5-80 microns and exhibits an intense, "sparkly," yellow-gold effect. Mearlin Sunset Gold differs greatly in appearance to the Inca Gold. This pigment is characterized by a very dark, metallic, reddish-gold lustre. Particle size range is 6-48 microns. Both Mearlin Inca and Sunset Gold can be used alone to achieve rich gold tones. Or, blending with other Mearlin golds to produce a broad spectrum range of unique gold shades such as white-golds, yellow-golds, red-golds, etc.

For further information Enter K103

'Haloflex' primer protects earthquake bridge

California's San Mateo-Hayward bridge, rebuilt after earthquake damage, has been coated with a high performance water-borne primer from ICI Resins. This compound, formulated with 'Haloflex' 202 vinyl acrylic terpolymer emulsion, provides the high level of corrosion resistance specified for near-coastal bridge and architectural structures.

Referenced PWB-145, the primer meets all California Department of Transportation (CALTRANS) corrosion protection standards and current 420 grams per litre VOC content regulations. The primer system will also meet projected 1992 standards of 340 grams per litre for this type of coating.

For further information Enter K104

Equipment

TRI-Spray launches Booth Master

Alkaline spray booth chemicals used to help break down paint and reduce the development of rust in associated water tanks have a certain drawback. In their concentrate form, they can cause severe burns, skin rashes and respiratory problems. The new Booth Master helps users comply with COSHH because an enclosed system is provided that automatically transfers chemical into the booth with operatives neither

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handling nor inhaling hazardous powders. There are only two occasions when an operator will handle the open chemical drum. Firstly, about once a month, when the empty 25-1itre drum is replaced (beneath the metering unit) and secondly, when the spray booth is drained and made up with fresh water in adding a small starting dose of chemical to the water tank. Booth Master is an enclosed automatic dosing unit. The equipment is programmed to suit the particular booth and a precise volume of chemical is always controlled.

For further information Enter K105

Ravas pallet truck scales

*D*arenth have introduced the RAVAS range of hand pallet truck scales and fork lift truck weighers.The basic model RPW-EC has a simple weight indication, whilst the RPW 3000 and RPW 5000 indicators have memory and parts counting facilities. The Explosion-proof model RPW 3000 EX is suitable for use in Zone I areas.

For further information Enter K106

Portable units detect static

*S*tatic electricity is an invisible hazard in a growing range of industrial handling, filling and sheet feeding processes, disrupting efficiency of operation, affecting cleanliness and quality, and posing a potential hazard to people and plant. It is particularly dangerous in areas where solvents are present. In the past two years, static electricity has been a suspected cause of over 200 fires in factory and commercial premises, with total damage of £85m.

Static electricity control specialists WLT Ltd have improved their range of portable devices which enable users to check whether static electricity is present, its magnitude and polarity. The FM300 is a new pocket-sized, fully automatic diagnostic device which provides a full data readout and a warning tone, indicating the presence of static on a

product or a processing machine. The FM300 has an integral battery test circuit, and will measure 0-50Kv.

The SS-2X designed for use in quality-sensitive and hazardous (EX) areas, has a measurement range of 0-200Kv, analog readout and, as an optional extra, a remote probe for inaccessible locations. It is equipped with a printer jackplug, enabling readings to be printed for product quality assurance and record purposes.

For further information Enter K107

New Contraves Euro-viscometers

*T*he two new Contraves instruments have been introduced by the Rheology Division of Mettler-Toledo: the Rheomat 108E and 108ER - operate to the German DIN 53019 standard. The portable, battery—powered Rheomat 108ER can be programmed to operate in a choice of six European languages enabling viscosity data to be collected and stored to a uniform standard at any plant or laboratory anywhere in
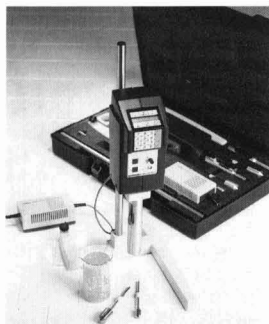
Europe. Both models provide either rapid spot meaurements at a selected shear rate or a ramp profile across a number of pre-selected shear rates. A computer connection port allows data to then be transmitted for printing out validation or statistical analysis. PC based software is available for data handling and, for the 108ER, provides full remote control of the meaurement programme.

For further information Enter K108

New Heraeus humidity cabinets

*H*eraeus Equipment Ltd have introduced a new generation of humidity test cabinets The 'HC' cabinet simulates both humidity and

temperature for capacities ranging from 50 to 1200 litres. All models offer fully automatic control by microprocessor/PC, easy compliance with extreme test cycles and an ergonomic design suited to the test laboratory. The cabinets also benefit from new asbestos-free mineral wool and the use of new refrigerants.
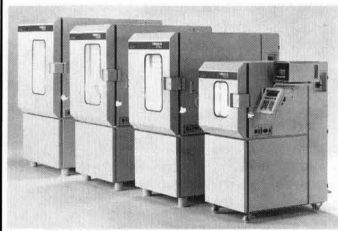
For further information Enter K109

Literature

US paint & coatings market to reach $20 billion by 1995

*T*he U.S. paints and coatings industry grew 6.4% annually during 1987 and 1989, from slightly over $11 billion to $12.6 billion. In gallons, growth was 3.6% per year for the industry. By comparison, the U.S. economy - as measured by GNP - grew 7.6% annually during this period. According to a study, Market Trends for Paints and Coatings, by the end of 1992, the total market for paints and coatings is expected to grow at a steady rate - from $12.7 billion to nearly $16 billion. This will represent average annual growth of more than 7% for 1989-1992. For the remainder of the forecast period. growth will average slightly more than 8% annually, bringing the market to the $20 billion mark by 1995. The study, published by Leading Edge Reports, a Cleveland-based market research company, discusses the industry in terms of four broad product groups: architectural coatings, product coatings for original equipment manufacturers, special purpose coatings, and miscellaneous allied paint products. Of the four market segments, growth was highest for special purpose coatings, which rose nearly 8% annually during 1987-1989. Product coatings enjoyed the next highest growth rate in 1987-1989 - 7.5% per year - followed by

ห้องสมุดกรมวิทยาศาสตร์บริการ

News

architectural coatings with average annual growth of slightly more than 5% annually. The average annual growth rate of approximately 4% experienced by miscellaneous allied paint products was the lowest among the four product groups during 1987-1989.

The study, Market Trends for Paints and Coatings from Leading Edge Reports contains numerous tables and graphs, and is available as a 122-page hardcover report for $1,700. The study is also available on IBM-compatible computer disk in ASCII format; the combined hardcover report plus disk sells for $1,850.

For further information Enter K110

European business directory

A six-language business directory of the world's largest market, Europe, has been published under the title "Europages". It lists the businesses which are representative of the European supply market - especially exporting companies. The eleven countries covered are: Belgium, The Netherlands, Germany, Luxembourg, Austria, Switzerland, Italy, Spain, France, Ireland, and the UK. All areas of key economic activity are listed and classified in 19 sections under 600 headings. It also contains statistical information on the European market, including some 500 tables, graphs and bar charts, together with a comparative economic analysis.

Indicatively, the section of "Europages" devoted to chemicals and pharmaceuticals, embraces organic and inorganic chemistry, petroleum fuels, industrial lubricants, paints and pigments, cosmetics and toiletries, basic pharmaceuticals and auxiliary products. Some 6,700 are listed in this section with full postal addresses, telephone and fax numbers.

Available in English, French, German, Spanish, Italian and Dutch, "Europages" is distributed free to purchasing managers throughout Europe and is designed to help small and medium sized companies, as well as large groups, in the run-up to the single European market in 1992.

For further information Enter K111

DECEMBER JOCCA WEATHERING

Meetings

Automotive coatings

A two day conference sponsored by PPCJ on Bonding and Coating Plastics in the Automotive Industry will be held at the Metropole Hotel, Birmingham on 21-22 November. For further details call 0737 768611.

Polymers and radiation

The 20th National Colloquium of the GFP: Polymers and Radiation will be held on 3-5 December at Montpellier, France. Topics covered include UV, EB curing. For further information contact: M. R. Sagnes, Laboratoire de Chimie Macromoleculaire, USTL, 34060, Montpellier Cedex, France.

People

Ciba-Geigy appoints Pigments General Manager

Michael Kerr has been appointed General Manager of Ciba-Geigy's pigments business in the UK. He was formerly Head of UK Marketing for Ciba-Geigy Pigments. Mr Kerr, who continues to be based at Clayton, Manchester, now has full responsibility for the business development, sales, servicing and profitability of all Ciba-Geigy's ranges of pigments in the UK and Eire. This appointment will help to create a clear identity of pigment operations for the UK market, distinct from the expanded role of Ciba-Geigy Pigments at Paisley, Renfrewshire, as the worldwide headquarters for 'Classical' pigments.

Changes at Tioxide UK Ltd

As from 1 July 1990, **Bob Rauch** has been transferred to become Business Development Manager of the newly formed Business Development Department, TUKL

Neil Reeves has been promoted to Technical Service Manager of Tioxide UK Ltd as from 1 July 1990.

Both will report to David Williams, Marketing Manager of TUKL.

Exxon Chemicals appointment

J. Malcolm Law has been named worldwide Vice President, New Business Ventures, for Exxon Chemical Company's Performance Products business group. The Performance Products business group is a major worldwide supplier of aliphatic, aromatic and oxygenated fluids, surfactants, petroleum additives and processing aids, synthetic alcohols and acids, and phthalate plasticisers for vinyl plastics.

Macpherson Industrial appointment

Macpherson Industrial Coatings has appointed **Bob Harris** as Group Technical Co-ordinator for water based coatings and will be based at Bromwich. Mr Harris has spent 25 years in the paint industry. In 1965 he joined Docker Brothers - later International Paints - in Birmingham and since 1971 has worked for the Macpherson Group at Bury, Aldridge and West Bromwich His main area of responsibility has been in water based coatings - both conventional and electro deposition types - for the industrial metal, wood and plastics markets. ∎

UV and electron beam curing

by Norman S. Allen and Michele Edge, Centre for Archival Polymeric Materials, Chemistry Department,
Manchester Polytechnic, Chester Street, Manchester M1 5GD UK

Introduction

Since its conception the radiation curing industry has become one of the most rapidly developing fields in the entire coatings industry. Several types of polymer systems suitable for curing by means of either high intensity ultraviolet (UV) or visible light or electron beam (EB) curing have been and continue to be developed. In so far as the polymer system is concerned both curing processes are essentially the same. To date several types of radiation curable prepolymers and monomers have been developed[1-4]. These are epoxy acrylates, acrylated oils, urethane acrylates, unsaturated polyesters, polyether acrylates, vinyl acrylates and polyene/thiol/silicone systems. The main objective in the preparation of these materials is to obtain a molecule which contains unsaturation capable of reacting with other unsaturated molecules when subjected to the irradiation conditions defined above to give a solid coherent film. Obviously, the molecules containing unsaturation must remain stable until the crosslinking reaction is required. This is normally achieved by the addition of 500-1000 ppm of an oxygen inhibitor or free radical scavenger such as paramethoxyphenol.

The popularity of radiation curable systems is associated with their following properties:
1) Consist of 100% reactive components i.e. no volatile solvents.
2) Energy efficient compared to conventional thermal curing.
3) Easily formulated.
4) Superior properties to those of conventional curing.
5) Variable viscosity to suit a particular application.

Application areas are now widespread and still growing and include plastics, metal, wire, textiles, wood, paper, laminates, resists, inks, adhesives and electronics. Depending on the viscosity of the system the resins may be applied through roller coaters, dipping, spraying or brushing. All these advantages combine to make UV and EB curable resins unique and in many cases superior to thermally cured systems with less complications.

There are two types of UV and EB curable systems. The first type are prepolymers and are functionalised resins which normally provide the photocured coating with its basic physical properties. The second type are monomers which are mixed with the prepolymers to provide final film properties and control the viscosity of the resin.

Prepolymers

The oligomers are functionalised for radiation curable systems by reaction with an acrylate such as acrylic acid or hydroxy propyl acrylate. A number of systems are commercially available in this regard such as:

      Epoxy acrylates
      Urethane acrylates
      Polyether urethane acrylates
      Polyester acrylates
      Polyether acrylates
      Acrylated oils

Other types of prepolymers include various water miscible systems, vinyl monomers, unsaturated polyesters, polyenes, thiols and silicones.

Thus, the reaction of an epoxy group with other acrylic or methacrylic acid will give rise to an epoxy acrylate (or methacrylate). There are a wide range of epoxy acrylates available including acrylates of bisphenol A glycidyl ether, acrylates of epoxidised oils such as Soya or Linseed and acrylates of epoxy Novolaks. The preparation of a simple epoxy acrylate is illustrated in Scheme 1 where R is a bisphenol A glycidyl ether[1].

Scheme 1
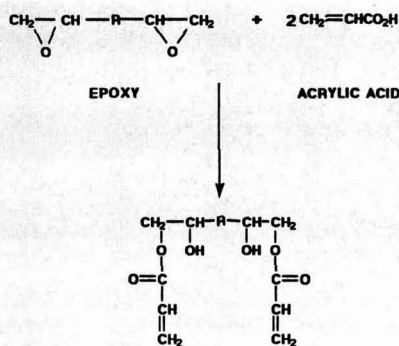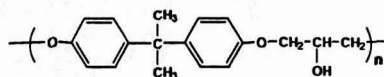
The reaction of an isocyanate group with the hydroxyl group of an acrylic or methacrylic monomer will give the corresponding urethane acrylates or methacrylates. The diisocyanates which may be used for this purpose have included tolylene diisocyanate (TDI), hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI) and diphenylmethane diisocyanate (MDI) while the monomers include hydroxyethyl acrylate, propyl acrylate and ethyl methacrylate. If other hydroxy compounds (e.g. polyethers, polyesters, polyols) are also present, which contain more than one hydroxyl group per molecule, then chain lengthening occurs giving a wide range of prepolymers which vary not only in functionality and molecular weight, but also in their final film properties[1].

Flexible urethane acrylates can also be made by the reaction of a diisocyanate with a long chain glycol. The half adduct of a diisocyanate acrylate may also be used. Aliphatic diol polyethers such as polyethylene glycols, polypropylene glycols and caprolactone polyols are widely used for this purpose as are polyesters with an excess of hydroxyl groups. As the flexibility increases the hardness, speed of cure and solvent resistance of the films decrease.

One weak link in the modification of many prepolymer systems is the use of a reactive diluent. Quite often this can give difficulties in the areas of odour, viscosity control, toxicity and equipment clean-up. Therefore, one possible route to overcoming these problems is to replace the reactive monomer with water which may be dried off prior to irradiation. There are two types of water based systems which

are (i) aqueous systems and (ii) aqueous emulsions. The first option is not favoured since the presence of water soluble acrylic functional components is likely to exacerbate rather than alleviate the toxicological hazards of the liquid coating. Using the emulsion technique polyesters and acrylics have been developed and are enjoying some commercial success particularly in the field of wood coatings. The epoxy and urethane acrylates prepared by emulsification have superior resistance properties compared with conventional aqueous based coatings systems. Some deterioration in performance compared with the standard UV curable coatings is possible due to the presence of the water sensitive emulsifiers and protective colloids in the final film.

Vinyl/acrylic prepolymers are another group which contain residual double bonds capable of further crosslinking. They can be prepared from vinyl or acrylic polymers by copolymerisation with monomers containing pendant acid, anhydride, hydroxy or glycidyl groups. Reaction of these groups with an unsaturated monomer is then possible. Vinyl double bonds may be introduced using a wide selection of compounds some of which are maleic anhydride, fumaric anhydride, itaconic anhydride, allyl alcohol, cyclopentadiene, acrylic acid, methacrylic acid, acrylamide, hydroxyethyl acrylate, glycidyl acrylate or glycidyl methacrylate. It is well known that the vinyl groups present in such compounds as

Scheme 2

$$\phi_2CO + RSH \xrightarrow{h\nu} \phi_2\dot{C}OH + RS\cdot$$

$$RS\cdot + CH_2=CHX \longrightarrow RSCH_2\dot{C}HX$$

$$RSCH_2\dot{C}HX + RSH \longrightarrow RSCH_2CH_2X + RS\cdot$$

$$RSCH_2\dot{C}HX + MCH_2=CHX \longrightarrow RSCH_2-CH{\left[-CH_2\,CH-\right]}_{M-1}CH_2\dot{C}HX \atop X \quad X$$
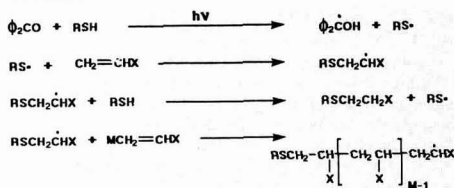
maleic anhydride are less responsive to UV than those based on acrylic acid. The following order of reactivity has been established[1]:

vinyl < allyl < methacrylic < acrylic

Unsaturated polyesters are another class which have been known for sometime and were one of the earliest systems used in radiation curing. Unsaturated polyesters can be broadly defined as condensation products of organic diacids and glycols. Unsaturation can be incorporated in a variety of ways to produce terminal, pendent and internal double bonds. Of these types, internal unsaturation provided by maleic anhydride is the most common. Other alternatives are stilbenes, cinnamates, allyl, acrylamide, norbornenyl, and acrylic. Whilst some of these types provide a reactivity advantage it tends to be reduced by slow copolymerisation with styrene. Replacement of styrene is generally economically unattractive, and this usually leaves the styrene-maleic systems in the most favourable cost performance position. Film properties can be changed, and improved through the selection and ratio of the acids and glycols and this is achieved only at an increased cost, and normally without an improvement in the rate of cure.

Polyene/thiol/silicone systems

Free radical addition of mercaptans to olefins has been known for many years. As presently understood, mercaptan olefin polymerisation occurs according to Scheme 2. W. R. Grace carried out much of the original work in this area and they are consequently very heavily patented[5-7]. This chemistry depends upon the rate of hydrogen transfer from mercaptan being competitive with the rate of olefin polymerisation. Olefin polymerisation would, of course, produce a vinyl polymer and an unreacted mercaptan.

In principle, this type of polymerisation affords some attractive alternatives as compared with acrylate polymerisation. The thiol-ene polymer can be regarded as a polysulphide, but, more importantly, if R in the above scheme is a urethane then one has an essentially thermoplastic urethane. Thermoset characteristics can be inserted by the addition of a trifunctional monomer or a trimercaptan. In contrast to the thiol-ene derived polymer an acrylic polymer results from vinyl polymerisation and the backbone remains fundamentally an acrylic polymer. In actual practice urethane acrylate oligomers do provide highly elastomeric polymers, but in some respects they probably are inferior to conventional urethane elastomers. In addition, to make a highly elastomeric urethane acrylate a relatively high molecular weight oligomer with an attendant high viscosity would be required. It would seem therefore that if the thiol-ene chain length is sufficiently long, then polymers comparable to conventional urethane elastomers could be produced. There are two advantages to the thiol/polyene systems. Firstly, they are non air inhibited and secondly flexible cured films can be obtained from a relatively low viscosity mixture without the need to incorporate a diluent.

Polyfunctional thiol compounds have been developed by W. R. Grace and these give very tough abrasive resistant coatings which are ideal for applications such as flooring compounds. It is also possible to modify acrylic UV curable formulations with polythiol polymers to improve their properties. Radiation curable silicone resins and monomers are now widely established with numerous applications requiring resistance to hydrolysis and heat, and possessing good sealant and mechanical properties. Coatings and optical fibres are one of the major applications.

Diluents/monomers

There are two types of diluents or monomers employed in radiation curable systems namely, reactive and non-reactive. Early monomers developed for radiation curable coatings in the late 1960's suffered from the fact that they were highly skin irritant. The types of monomers employed were monofunctional (containing one double bond per molecule) and multifunctional (containing two or more double bonds per molecule). The reactive monomer or diluent plays several important roles in the UV and EB curing of coatings such as the determination of the cure rate in conjunction with the photoinitiator system, film properties which are to some extent dependent on the type of monomer employed and control of adhesion and flexibility.

Examples of the early monomers used include the following mono and difunctional products. These first generation monomers may be monofunctional such as 2−ethyl hexyl acrylate, difunctional such as hexanediol diacrylate and trifunctional such as trimethylol propane triacrylate the fist two of which exhibit strong characteristic odours and the third are little used. Methacrylic analogues are also available but they suffer from the disadvantage of having slow reactivity, as a result of oxygen inhibition and also exhibit strong odour. The only major area where the methacrylates are used is in the UV adhesive industry.

Major raw material suppliers have, since the 1960's, developed new monomers which have low Draize values and are widely used in radiation curable coatings. These low Draize second generation monomers can be mono-, di- or tri-functional. For example, a typical difunctional type is prepared by reacting one mole of a diol e.g tripropylene glycol with two moles of acrylic acid. Examples are shown in structures I-III.

Vinyl functional monomers may also be used such as vinyl toluene and styrene but they are slow curing. These are usually incorporated with unsaturated polyesters for wood

Tripropylene glycol diacrylate (TPGDA)

$$CH_2=CH-CO-O-(CH_2CH_2CH_2O)_3-CO-O-CH=CH_2 \qquad I$$

Dianol Diacrylate (CDDA)

$$(CH_2=CHCO-O-CH_2CH(OH)CH_2-O-p-C_6H_4-p-)_2C(CH_3)_2 \qquad II$$
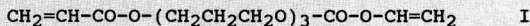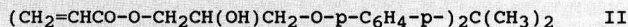
Glycerol Propoxylate Triacrylate

$$CH_2=CHCO-(O-CH_2-CH(CH_3))_n-O-CH(CH_2-O-(CH(CH_3)CH_2-O-)_n-CO-CH=CH_2)_2$$

III

coatings' application areas. Both are used because of their low cost but suffer from the disadvantage of giving odour on the production line. N-vinylpyrrolidone (2NVP) is far more important because of its higher reactivity and good viscosity reducing powers when used with other acrylate monomers. 2-NVP can also be used as a water soluble monomer with water based oligomers as well as flexible coatings because of its low shrinkage value. However, it suffers from the disadvantage of being costly and having high odour.

The non-reactive monomers are divided into solvent and plasticiser types. The solvent dissolves the prepolymer and is then flashed off prior to curing after application to the substrate. The role of the solvent is to act as a carrier for the prepolymer as well as a viscosity reducer for application purposes. The concentration of solvent employed in a UV coating can range from 5-50% depending on the type of application. Low levels of solvent employed in the coating can be absorbed into the substrate or can be flashed off by the infra-red present in the lamps used. High levels of solvent in the coating, especially when applied as a thick coating, will lead to the necessity of flashing off the solvent before passing under the UV lamps. High levels of solvent can also influence the properties as well as the gloss level of the film. The role of the plasticiser is to modify tack, viscosity, flexibility and hardness of the cured film.

Amine synergists

Amine synergists are used in conjunction with photo-initiators to accelerate the rate of cure when incorporated into UV formulations. These are prepared by the Michael addition of a secondary alkyl, aryl, aliphatic or acyclic amine to an unsaturated acrylate group. A typical structure of an amine synergist is shown in Structure IV.

$$CH_2-O-CO-CH_2-CH_2-N(C_2H_5)_2$$
$$|$$
$$CH_2=CH-CO-O-CH_2-C-CH_2-CH_3$$
$$|$$
$$CH_2-O-CO-CH=CH_2$$

IV

These monomers are usually mixed with oligomers in formulations between 8-20% by weight.

Photocuring mechanisms

In order to induce the photopolymerisation or photocross-linking of an acrylated system two types of initiators are available. The first induc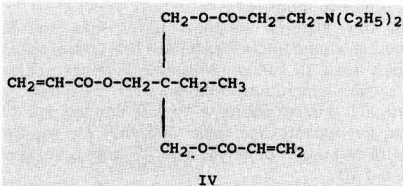es a free radical chain process in which low molecular weight monomers and prepolymers are converted by absorption of ultraviolet or visible light into highly crosslinked and chemically resistant films. The second type of initiator polymerises via a cationic mechanism and has the advantage in this respect of being oxygen insensitive. Both these processess will be considered here[1,8-13].

The basic mechanism for any free radical photocurable system is shown in Scheme 3. In the first step the photo-initiator absorbs light energy followed by a subsequent reaction to give a radical initiator (R.). The radical initiator will then induce a chain reaction or more commonly a chain growth polymerisation where the rate of propagation is k_p. In the absence of oxygen termination will occur by a radical coupling process or disproportionation with rate k_t[14].

Scheme 3

$$Initiator \xrightarrow{\hspace{2cm}} 2R\cdot$$

$$R\cdot \; + \; M \xrightarrow{\quad k_p \quad} RM\cdot$$

$$RM\cdot \; + \; M \xrightarrow{\quad k_p \quad} RM_2\cdot$$

$$RM_n\cdot \; + \; M \xrightarrow{\quad k_p \quad} RM_{n+1}\cdot$$

$$RM_n\cdot \; + \; RM_m\cdot \xrightarrow{\quad k_t \quad} RM_{n+m}R$$

$$RM_n\cdot \; + \; RM_m\cdot \xrightarrow{\quad k_t \quad} RM_nH \; + \; RM_n(-H)$$
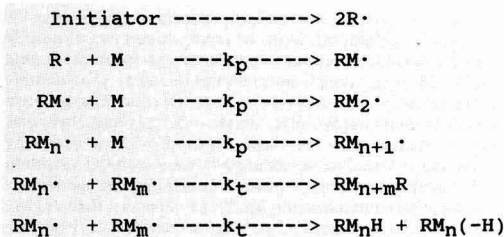
Application of steady-state kinetics results in the following expression for the rate of polymerisation:
$$Rate = k_p[M](\varphi)_R I_a/k_t)^{1/2}$$
where φ_R is the quantum yield of free radicals produced and I_a is the intensity of light absorbed by the initiator. It is seen that from this expression the rate is dependent upon the square root of the light intensity absorbed by the system and is a consequence of the bimolecular termination reactions. There-fore the photochemistry of the photoinitiator is extremely important and should possess the following properties[1-14]:
(1) High absorptivity in the region of activation which is usually 300-400 nm with a high extinction coefficient. This is normally dependent on the application.
(2) High quantum yield of free radical formation.
(3) Adequate solubility in the resin system.

(4) High storage stability and not adversely affect the resin.
(5) Odourless and non-yellowing.
(6) Non-toxic and this also applies to its products of irradiation.
(7) Ease of handling.

There are two basic categories of photoinitiators which meet these requirements. The first group are the hydrogen atom abstracting type photoinitiators and are normally, aromatic ketones, diketones and quinones. Some typical structures are benzophenone (V), thioxanthone (X=S) or Xanthone (X=O)(VI), anthraquinone (VII) and benzil (VIII). Benzophenone and thioxanthone are also available in various substituted forms. Thus, chlorine, alkyl, alkoxy or aryloxy groups in benzophenone at the para position will enhance the absorptivity and activity of the molecule[5-15]. The same applies to substitution in the 2-,3- and 4-positions of thioxanthone[16-20]. For aqueous based systems water solubilising groups may be present such as sodium alkylsulphonates or trimethylammonium sulphonate or chloro salts[21]. Thioxanthone photoinitiators have absorption maxima above 380 nm and therefore are especially useful for white pigmented resins where most of the UV region below 380 nm is screened by the pigment.

benzophenone

V

VI   X = O, S

R = Alk, OAlk, OAlk—SO$_3^-$M$^+$, OAlk—N$^+$—Z$^-$, Cl

VIII

VII
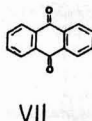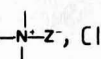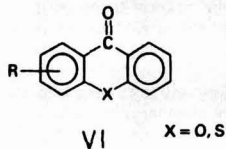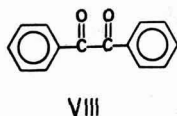
The second class of photoinitiator is the photofragmentation type which undergo a cleavage reaction to produce free radicals capable of inducing polymerisation. Examples of such structures are the benzoin ethers (IX), benzilketals (X), α,α-diethoxyacetophenone (XI), α-hydroxyalkylphenones (XII), benzoyl oximes (XIII), acylphosphine oxides (XIV), acylphosphonates (XV) and peroxy compounds such as derivatives of dibenzoyl peroxide (XVI and XVII)[8-14].
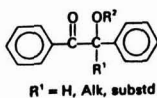
R^1 = Ar, t-Bu; R^2, R^3 = C$_6$H$_6$

XIV

R^1 = Ar, t-Bu; R^2, R^3 = Alk

XV

XVI
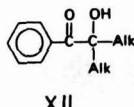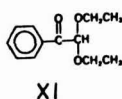
XVII
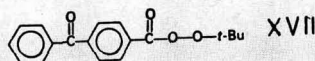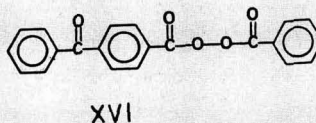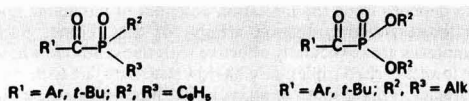
The first class of photoinitiators undergo a primary process of hydrogen atom abstraction from the environment to produce a ketyl and corresponding alkyl radical[22]. The reaction usually occurs from the lowest excited triplet state of the ketone or quinone and depends on the intersystem crossing rate (isc), the configuration of the triplet state and its corresponding energy. The photoreductive ability of the environment is also an important factor and is related to the carbon-hydrogen bond strength of the species donating the hydrogen atom. Commercial prepolymers and diluent monomers contain readily abstractable hydrogen atoms with alcohols and ethers being particularly effective in this regard. A typical example is benzophenone shown in Scheme 4 which absorbs UV light within the wavelength region 300-400 nm and undergoes efficient intersystem crossing to its lowest excited triplet state. The latter abstracts a hydrogen atom from the environment (RH) to produce corresponding ketyl and alkyl radicals respectively[11-14,22]. The ketyl radicals couple to produce pinnacol while the alkyl radical is believed to act as the initiator of polymerisation and/or crosslinking. In the case of quinones a semiquinone radical is produced which undergoes disproportionation to regenerate the original quinone and a quinol.

The efficiency of carbonyl photoinitiators may be enhanced through the use of a tertiary amine cosynergist and these are available in a variety of forms. Here the excited triplet state of the ketone forms an intermediate excited electron-transfer complex (ET) with the tertiary amine, often referred to as an exciplex as shown in Scheme 5[22-25]. The exciplex is stabilised by charge-transfer, because of the low ionisation potential of the amine donor. The efficiency of such complex formation

R^1 = H, Alk, substd Alk;   R^2 = H, Alk, substd Alk

IX

—CO—R^3, —SO$_2$R^3; R^3 = Alk, Ar

R^1, R^2 = Alk, substd Alk

X

XI

XII

R^1 = Ar; R^2 = Alk, Ar; R^3 = Alk, substd. Alk, Ar, OAlk

XIII
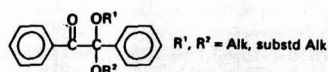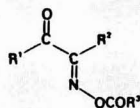
also depends upon the ionisation potential of the amine and the corresponding electron affinity of the ketone. Such complexes are particularly effective with thioxanthone where the lowest excited triplet state has low reactivity due to its $\pi\pi^*$ character. Triplet states of aromatic ketones which are $n\pi^*$ in character have a high affinity for intermolecular hydrogen atom abstraction[22].

Scheme 4

```
Ar₂C=O ---hv------> Ar₂C=O¹ --isc----> Ar₂C=O³

Ar₂C=O³ + RH -----> Ar₂Ċ-O-H (Ketyl) + R·

2Ar₂C-O-H --------> Ar₂C(OH)-C(OH)Ar₂ (Pinnacol)

R· + CH₂=CHX -----> RCH₂-CHX· -------> Polym.
```

Scheme 5

The use of the tertiary amine may take one of a variety of forms. These may be as in the case of the amine diacrylate resin shown in Structure IV above or as a solid amine in the case of ethyldiaminobenzoate (Structure XVIII) or as a substituent in the initiator chromophore such as 4,4'-bis (diethylamino) benzophenone, often referred to as Michler's ketone (XIX). The latter is no longer used due to its carcinogenic property and the use of liquid amines can result in diffusion problems from the coating and loss of gloss and adhesion[1].

X VIII

XIX
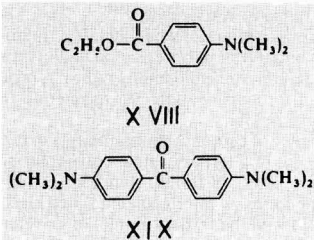
The second class of photoinitiators undergo direct photo-fragmentation in the excited state into free radicals as shown in Scheme 6 for a benzoin aryl ether[26,27]. The nature of the excited state responsible is uncertain since typical triplet quenchers do not influence the reaction. Depending upon the structure of the molecule scission may occur in the α- or β-positions. Benzoyl and benzyl type radicals are produced from the α scission process and both are believed to be involved in initiating polymerisation of an acrylic monomer.

Scheme 6

Oxygen inhibition in UV curing with free radical photo-initiators is a particular problem which has been the subject of much activity in recent years. The main problem is two fold. The first, is that the lowest excited triplet state of many ketonic photoinitiators is qu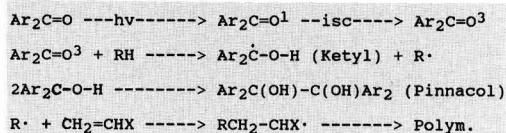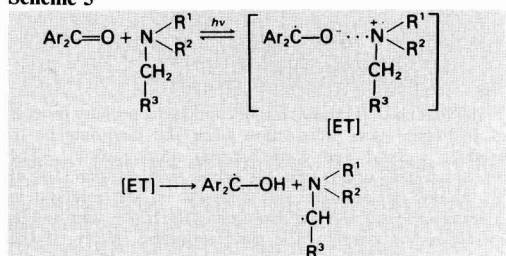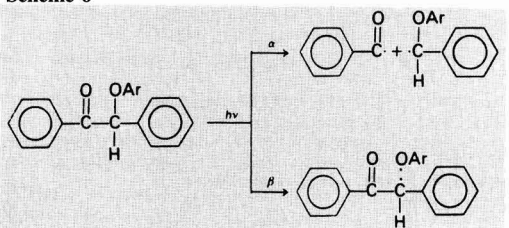enched by oxygen. The second is that free radicals arising from the initiation process may also be quenched. The exclusion of oxygen has been undertaken effectively through nitrogen blanketing, although expensive, and through the use of transparent foils[28] and paraffin waxes[29]. In the latter case the wax forms a thin oxygen barrier on the surface of the coating. The use of tertiary amine synergists impair the quenching effect of oxygen and this is believed to be due to the ability of the α-aminoalkyl radicals in Scheme 5 above to react with oxygen to generate peroxy radicals[11-14,30]. Thiol and phosphite compounds are also effective in scavenging oxygen and are sometimes added to commercial prepolymers and diluent monomers[11]. The use of oxygen insensitive photoinitiators is another more recent method. Alkanesulphonic acid esters of α-hydroxy-methylbenzoin and its ethers are claimed to be oxygen insensitive as are the use of combinations of a photofragment-ing type initiator with a hydrogen abstracting type[11,31,32]. The latter combination provides sacrificial free radicals for reaction with oxygen and allows the hydrogen atom abstrac-tion reaction to proceed uninhibited. Surface active photo-initiators based on a surfactant type structure are also claimed to be particularly effective[32].

In contrast to the free radical type photoinitiators cationic photoinitiators have been developed in more recent years for the polymerisation of epoxy and vinyl-ether resins. Depend-ing on the structure these initiators are capable of producing either Lewis acids such as BF_3 and PF_5 or Brφnsted acids such as $H+BF_4-$ and $H+PF_6-$. In the early stages of develop-ment aryldiazonium compounds were used to generate the Lewis acids[12,13]. However, these were found to be very unstable and produced nitrogen on curing which released bubbles into the resin films. To overcome these problems more stable diaryliodonium and triarylsulphonium and sele-nonium salts have been developed. On photolysis these compounds produce strong Brφnsted acids $(H+X-)$ where X is usually a tetra- or hexafluoro substituted salt such as PF_6-, SbF_6-, BF_4- or AsF_6-[33]. These are shown in Scheme 7 for the sulphonium salt where the acid readily reacts with the monomer M in order to induce polymerisation. Termination usually occurs through impurities. However, in the absence of impurity centres living polymers are produced. Many other types of effective cationic type photoinitiators are now available especially the most recently introduced mixed ligand arene-cyclopentadienyl metal salts of complex metal halide anions[12,34,35].

Many workers consider the cationic type photoinitiators to be superior to those of the free radical type. In particular, they are insensitive to oxygen quenching, are readily sensitised by the use of dyes[33,36] in the visible region of the spectrum and may be post-thermally cured. It is noticed in Scheme 7 that free radicals are also produced and these have been found to induce the photopolymerisation of acrylated resins. Indeed mixed acrylate and epoxy-functional resins may be cured with these types of photoinitiators either alone or more desirably in conjunction with the free radical types. In the latter case the effect of oxygen inhibition is overcome. Such systems have aquired a new terminology called 'hybrid' systems[12].

Scheme 7

```
Ar₃S⁺X⁻ + RH --------hv-----> Ar₂S + Ar· + R· + H⁺X⁻

H⁺X⁻ + M        ---------------> HM⁺X⁻

HMₙM⁺X⁻ + M     ---------------> HMₙ₊₁M⁺X⁻

HMₙM⁺X⁻ + Impurity ---------> Polymer
```
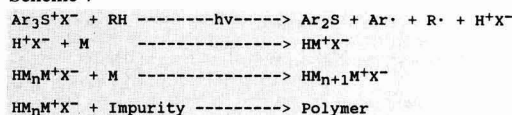
Electron beam curing technology

Electron Beam curing technology is closely related to UV curing technology with respect to the raw materials which can be used to provide the cured coating[37,38]. The development of electron beam curing, however, has lagged behind that of UV curing due to the lack of suitable electron accelerators which need to be compact and inexpensive[39]. The capital cost of electron beam curing equipment is far greater than that for UV curing although this cost has reduced in recent years with the introduction of new accelerators[1,39,40-42]. Consequently electron beam curing has become a viable process in a number of applications which have been dominated by UV curing or conventional coatings techniques. There are now a wide range of applications in which electron beam curing techniques are used[43,44].

The basic concept of electron beam curing is the use of high energy electrons to induce free radical polymerisation[45]. Electron beam curing systems are designed to allow the unpolymerised coating to pass beneath an electron source at varying rates in order to facilitate polymerisation. This technology will be elaborated on further in the following sections.

Electron beam accelerators

An electron beam accelerator can be regarded as a vacuum triode in which low velocity electrons are produced at the surface of the cathode or a filament by applying a current and accelerated to the anode by application of a high sensitive voltage[40-42,45]. An electric or magnetic focusing device is used to ensure maximum concentration of electrons at the intended surface. The electrons emitted from the cathode the individual full charge of the accelerating potential in eV as they strike the anode. The electron density is controlled by the amperage passing through the cathode. This process of producing accelerated electrons is carried out in a vacuum, which is maintained while allowing for the efficient transmission of electrons by a thin metallic window usually made of titanium or aluminium foil. The electron beam passes through this window and strikes the substrate to be cured, which is blanketed under nitrogen. At the present time there are two basic types of electron beam curing accelerators commercially available; the scanned beam and electron curtain types[37-39,42,45].

Scanned beam accelerators

The basic design of this type of accelerator is illustrated in Figure 1. The electrons are produced at a pointed cathode and are accelerated towards the anode. This produces a narrow beam of electrons which are scanned across the direction of the substrate by an electromagnetic scanning device. These scanned beam accelerators can have a single or multistage electron accelerator. The single stage acceleration is used for accelerating voltages of less than 250 KV. The multistage accelerator is used for accelerating voltages in excess of 250 KV.

Electron curtain accelerators

The basic design of this type of accelerator is illustrated in Figure 2. This accelerator uses a linear filament type of cathode which is in the centre of a cylindrical vacuum chamber. The electrons emitted from the cathode are accelerated over a single stage to pass through the metallic window producing a continuous stream (curtain) of electrons along the length of the filament. This type of accelerator is used for accelerating voltages between 150-300 KV and is generally cheaper than the scanning beam accelerators.

Figure 1
Schematic diagram of a Scanned Beam Electron Beam Accelerator.
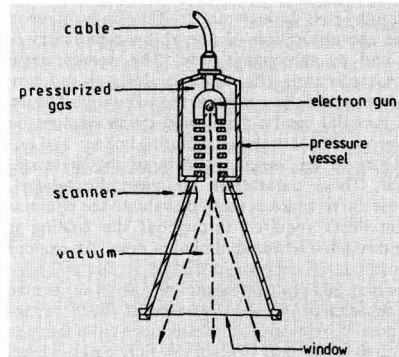
Figure 2
Schematic diagram of an Electro-curtain Electron Beam Accelerator.
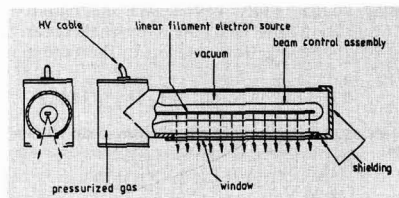
Operational conditions

With electron beam curing there are a number of parameters which need to be considered and defined with regard to the efficiency of the curing process and operational conditions such as dose, electron energy and penetration, electron energy losses and back scatter effects.

Dose

The radiation dose is the amount of energy absorbed per unit mass of material. The unit used to measure an absorbed dose of electron energy was formerly the rad. This unit is defined as the absorption of 100 ergs of energy per gram of sample. The megarad (10^6 rads) is the practical unit commonly used in electron beam curing. However, there is a newer international unit being adopted for dose; namely the gray (Gy) which is equivalent to 100 rads or 1 JKg^{-1} [38]. In practice the absorbed dose of energy is calculated from a formula that is empirically derived for the particular electron beam curing unit. This formula usually takes the following form:

$$D = K \times I/V$$

where D=dose in megarads

I=beam current in milliamps

V=line speed in ft/min

K=constant (Equipment dependent)

The constant K is derived for the particular electron beam curing equipment in use and takes into account energy losses for that particular electron beam curing unit. It is sometimes quoted as the dose rate per unit time, however, this is not a term in common use.

Electron energy and penetration

It is the nature of electron beams that they lose their energy as they pass through matter. This is advantageous as it results in the absorption of energy in a radiation curable coating and its subsequent cure. The energy absorption throughout a coating (its depth in dose) is not however, uniform because of this continual loss of energy. The depth to which a material can be penetrated by an electron beam is directly proportional to the accelerating voltage and inversely proportional to the specific gravity of the material being irradiated. These parameters are generally related by a depth-dose curve which is used to evaluate the minimum and maximum doses required throughout the coating usually working through a required minimum dose. An example of a depth-dose curve is shown in Figure 3. The 300 KV curve indicates that this electron beam has lost all of its energy in passing through a unit density material 0.025 inches thick $(0.0625 \text{ g cm}^{-2})$. However, as can be seen from the graph the surface of the coating is likely to be fully cured whereas the bottom of the coating is likely to be appreciably undercured due to the relatively small dose received by this area of the coating. It is necessary therefore, to consider dose uniformity, which involves selecting a maximum and minimum dose level acceptable for curing and then selecting an accelerating voltage which will deliver the required dose range. The ideal situation is to obtain the smallest percentage variation of dose going from the top to the bottom of the coating.

Figure 3
Depth versus dose curves for an Electro-Curtain electron beam curing equipment.

Energy losses

Since an electron beam loses its energy on passing through matter, the most likely source of energy loss in electron beam curing equipment is at the titanium or aluminium window. Although the windows are very thin (0.05 mm) they are made of relatively high density material. The consequence of this energy loss is the product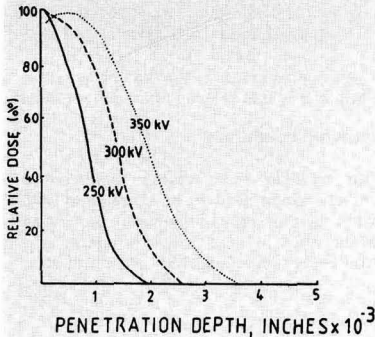ion of X-rays by interaction of the accelerated electrons with the electron shells of the elements in the window. There are basically two types of possible interactions producing either a Bremsstrahlung or a characteristic X-ray. The Bremsstrahlung occurs when accelerated electrons are within the Coulomb field of an atom core. This causes a deflection from their original direction with a consequent loss of kinetic energy. This loss in kinetic energy is then emitted in the form of photons. Since there are a number of separate coulombic interactions possible for each accelerated electron there are a number of photon energies emitted. The Bremsstrahlung is therefore a continuous spectrum. The characteristic X-ray is produced when an electron is ejected out of an inner shell of the metal atom.

The vacancy produced is then filled by electrons from higher shells and the energy differences which then occur are quantised and are emitted as X-rays with characteristic energies producing a linear spectrum. The graph shown in Figure 4 illustrates the relationship between beam energy loss and operating voltage at a typical titanium foil window. It can be seen that low operating voltages beam energy losses are high whereas at high operating voltages the beam energy losses are low.

Energy can also be lost in the air gap between the foil window and the substrate. As with window losses, these energy losses are more pronounced at lower accelerating voltages. However, these losses are much smaller than those occurring at the window. If a unit was operating at 125 KV then the 125 KV curing beam would experience an approximately 40% energy transfer loss with 30% occurring at the window and 10% in the air gap.

Figure 4
Percentage energy loss at the titanium window versus operating voltage for an electro-curtain electron beam curing unit.
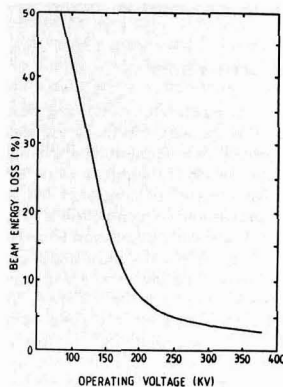
Backscatter effects

The concept of 'backscatter' is illustrated in Figure 5[46]. The effect is produced when an energetic beam of electrons strikes a substrate with significant density to deflect some of the electrons back into the coating. These deflected electrons have lost energy by the time they are deflected so their penetration potential is less than the original beam. However, they do account for an additional dose delivered within the bottom portion of the coating. The backscatter effect will depend on the substrate material, its thickness and its density. If the effect is pronounced it could result in cure being achieved at lower accelerating voltages thus saving energy. This effect is readily adaptable to thin coatings and thin substrates when the equipment utilises a backscatter plate (see Figure 6).

Figure 5
Electron beam backscatter.

Figure 6
Use of backscatter plate in electron beam curing.

In this application the electron beam passes through the coating and the substrate to strike a backscatter plate and passes back through the substrate and coating thus delivering a second albeit reduced dose of electrons.

Mechanism of electron beam curing

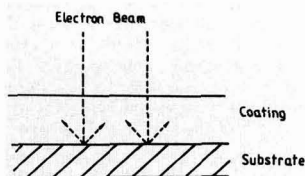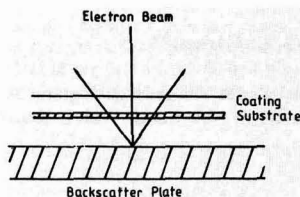The mechanism of electron beam curing is fundamentally different from that of UV curing. The latter requires the use of photoinitiators which are activated by UV or visible light with energies in the range 3-6 eV whereas electron beam curing is a consequence of the direct interaction between radiation and monomer in the energy range 150-500,000 eV[1,45,47]. Since chemical bond energies lie in the range 1.5 to 8.5 eV it is obvious that UV initiation results in specific bond rupture whereas electron beam initiation results in an unpredictable pattern of bond scission.

Thus, on exposure of an organic coating to an accelerated electron beam an exchange of energy takes place in which the kinetic energy of the electron is transfered to the absorbing medium. This encounter sets up a coulombic interaction which results in several pathways of producing highly reactive radicals capable of initiating polymerisation. The exact mechanism of energy transfer and production of energised molecular species are unknown and likely to be highly complex. Gaseous phase mass spectroscopy has been used as a model to elucidate the processes that take place in the condensed phase as in a curable coating. There are two basic primary processes which can occur namely, ionisation or excitation. Electron impact can give rise to ionisation with molecular ionic and molecular radical formation through fragmentation (Scheme 8).

Scheme 8

$$AB + e^- \longrightarrow AB^+ + e^-$$
$$\downarrow$$
$$A^+ + B\cdot$$
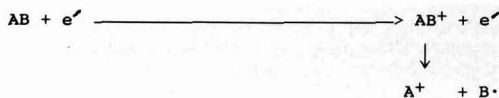
Molecular excitation may also occur thus:
$$AB + e \longrightarrow AB+$$
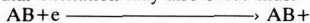
These primary species can now undergo a number of secondary processes such as recombination or further ionisation resulting in slower electrons. The secondary processes as shown in Scheme 9 can occur.

The radicals produced are believed to be the initiating species whereas the ionic species are believed to play a minor role in initiation and undergo rapid recombination reactions by electron capture and charge neutralisation. Radical formation can be enhanced by including specific atoms in the medium. For example, as represented above is favoured for molecules containing halogen atoms or cyano groups. However, aromatic molecules act as electron traps resulting in low radiation yields. With a high intensity electron beam a very high local concentration of free radicals is formed in the

coating. This results in an inefficient conversion of radiation energy to chemical energy because a large percentage of the free radicals recombine instead of initiating the curing process. This problem can be overcome by making use of several passes or by pulsing the electron beam. Some workers have studied the effect of electron beam dose on the rate of double bond disappearance in an unsaturated polyester/styrene solution (65/35%)[48]. They found a linear increase in the rate of double bond disappearance with an increase in the dose rate up to about 20 MRads/min. At high rates this decrease in unsaturation levelled out and then decreased slightly up to 85 MRads/min.

Scheme 9

$$AB + e^- \longrightarrow A\cdot + B\cdot$$
$$AB^+ + e^- \longrightarrow AB^*$$
(electron capture)

$$AB^+ + CD^- \longrightarrow AB^* + CD^*$$
(neutralisation)

$$AB^+ + CD \longrightarrow ABC^+ + D\cdot$$

$$AB^+ + AB \longrightarrow AB_2^+ + A\cdot$$
(intermolecular energy transfer)

$$AB^* \longrightarrow A\cdot + B\cdot$$
(molecular dissociation)
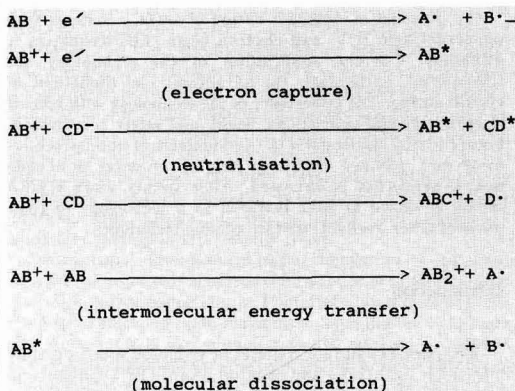
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UV and EB Curing

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Abstract

The potential of radiation curing of surface coatings with ultraviolet light (UV) and electron beam (EB) techniques is discussed. Current applications of the technology are summarised, particularly the advantages and limitations of UV/EB curing. The importance of the technology with respect to environmental restrictions, health and safety is evaluated. Future trends, particularly the development of novel processes using new polymer chemistry yielding products possessing unique properties is discussed. After twenty years UV/EB curing is shown to have matured as a technology to complement other available surface coating techniques.

Introduction

The curing of surface coatings by radiation sources mainly ultraviolet light (UV) and electron beams (EB) continues to be a field of intense commercial activity[1-6]. In this respect UV/EB curing complement the other technologies available, possessing certain advantages and yielding novel products not capable of being readily achieved by other methods. Developments with the technology continue to be publicised at major international conferences particularly the RadTech meetings and the International Meetings on Radiation Processing, the most recent of which were held in Chicago and Holland respectively. The growth rate in the field is currently believed to be 30% per annum[7], the reason for such growth being attributed to a variety of environmental, economic and technical advantages, particularly in those industries where the technology is most popular, for example the graphic arts (printing), timber (finishing) and electronics (coatings). The current value of such coatings has been estimated at US $400M per annum for both US and European markets respectively. Combined, UV and EB curing still only represent a small portion (~3% in the US) of the total market for coatings, largely due to the major limitations and constraints of the technology. However recent research has become increasingly successful at overcoming these limitations by utilising novel chemistry and equipment design. The technology has now reached the point where it is relevant to virtually all materials used in every day life. Numerous reviews and books have been written on UV/EB curing[1-6]. The present article will summarise the basis of the technology with a brief overview of more recent developments, applications and future trends in surface coatings and related fields.

The technology

Radiation curing involves rapid polymerisation of a monomer/oligomer mixture to give a film which can also be crosslinked. In UV systems, fast rates of polymerisation are achieved with the aid of photoinitiators and high performance (up to 400 W per inch) lamps. In EB, self-shielded electron beam processors with energies up to 400 keV are utilised for this same purpose. With respect to the resin systems used in these curing processes (Table 1), the basic component is the

Table 1
Typical W/EB Formulation

Composition	%
Resin	40-50
Reactive diluent	40-50
Photoinitiator (UV)	5-10
Surfactants, additives	0.5

oligomer which is essentially a prepolymer of low molecular weight (~3000) and is commonly a urethane, epoxy or polyester acrylate, although non-acrylated oligomers are also being progressively introduced. The oligomer is usually viscous and requires the addition of monomers as reactive diluents, not only to adjust the rheological properties of the resin for application, but also to speed up the cure by crosslinking. The structure of the reactive diluent is critical in determining the properties of the finished film, such as flow, slip, wetting, swelling, shrinkage, adhesion and migration within the film. The reactive diluent can be either mono-functional or multifunctional, the latter being preferred because of enhanced crosslinking during cure. The properties required in the choice of reactive diluent are solubility, odour, ability to reduce viscosity of the medium, volatility, functionality, surface tension, shrinkage during polymerisation, glass transition (Tg) of the homopolymer, effect on speed of overall cure and toxicological properties. Monomers with low skin irritancy as determined by the Draize rating[8-9] which should not be above 3 are recommended. Typical of the monomers used as reactive diluents in these systems is tripropylene glycol diacrylate (IPGDA, I) which possesses good solvency for many of the prepolymers, a currently acceptable Draize rating, relatively low viscosity, high speed of cure and good viscosity reduction properties.

$$CH_2{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}(C_3H_6O)_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH{=}CH_2$$

(I)
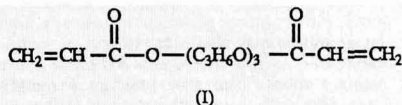
Chemistry of curing

Whilst the chemistries of EB and UV curing are related, one of the essential differences is the need for inclusion of photoinitiators in UV systems to achieve fast cure. Thus, with UV, there is the possibility that unreacted photoinitiator contaminates the cured film. Both UV and EB currently use acrylates as the predominant chemistry although, particularly with UV, recent developments as described below now involve vinyl ethers or epoxies.

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EB Systems The principles of this technique involve curing a monomer/oligomer mixture by exposure to electrons in a low energy EB machine. Under these conditions, both radical and ionic species are formed (Equations 1-5, where RH is a simple monomer or oligomer, e_p is the impinging primary electron, e_s represents a low energy electron (1-2 eV) removed from RH or produced from ep by collisional loss of kinetic energy and e covers electrons with energies between e_p and e_s).

$$RH \longrightarrow R^{\cdot} + H^{\cdot} \tag{1}$$

$$RH + e_p \longrightarrow RH^+ + e_s \tag{2}$$

$$RH + e_s \longrightarrow RH^- \tag{3}$$

$$RH + e \longrightarrow R^- + H^{\cdot} \tag{4}$$

$$RH + e \longrightarrow R^+ + H^- + e \tag{5}$$
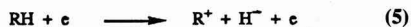
Most EB curing reactions are believed to occur predominantly through free radical processes with minimum participation of ions. The presence of moisture and the fact that curing in most films occurs at temperatures above 25°C has previously led researchers to believe that the role of ions in these processes was suppressed. Recent developments have indicated that ionic processes may participate under certain conditions in curing. Firstly, the availability of a new class of low energy EB machines capable of delivering exceptionally high doses in short periods of time are now operational in the market. These machines are capable of delivering 1500 Mrad m/min, i.e. 1 Mrad at 1500 m/min or more conveniently 3 Mrad at 500 m/min. The rates of reaction of free radical processes are directly proportional to [dose rate]$^{0.5}$ as a maximum, whereas for corresponding ionic processes rates of reaction are directly proportional to dose rate. Thus high EB dose rates as delivered by the latest machines should favour ionic processes[10]. Secondly, in basic work involving the sophisticated technique of fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) where the primary effects of electron bombardment on monomers has been investigated, ion formation in monomer

Figure 1

Mass spectra of TPGDA widl magnetic (VG) and FIICRMS (FT) instruments: (a) Chemical Ionisation VG (argon), (b) Chemical ionisation FT, 1 second, (c) Chemical ionisation FT, 60 seconds

systems is facile[10]. Using a typical multifunctional acrylate as monomer eg. TPGDA, oligomerisation reactions involving this monomer in the FTICRMS are readily observed (Figure 1). In this figure species at m/z 359, 413 and 502 are progressively formed with intensities which increase with increasing residence time of the molecule in the ion source. Such oligomerisations are due to ion molecule processes (Equation 6) where R is a fragment of the monomer TPGDA (M).

$$R^+ + M \longrightarrow RM^+ \tag{6}$$

Using the FTICRMS technique, both cationic and anionic oligomerisation reactions are observed with monomers such as TPGDA which are used extensively in EB curing reactions. The importance of observing ionic processes in EB curing is two fold. Firstly, since ionic and free radical processes can yield products possessing different structures and therefore different properties, it is important to be able to optimise each of these mechanisms in any curing system. Thus from the same oligomer/monomer mixture cured by EB, it may be possible to obtain a different product depending on the method for optimising either the ionic or free radical process. The other significant feature of ionic processing is that air inhibition is no longer a problem thus inerting with nitrogen is not required with subsequent economic savings in EB running costs.

UV Systems – Free Radical In the chemistry of UV curing, fast polymerisation is achieved with the use of photoinitiators and high performance lamps. Photoinitiators which produce both free radical and cationic intermediates are used although the former types are more frequently applied in current commercial applications. Photogeneration of free radicals can be achieved in two ways. The first is an intramolecular process involving fragmentation of a photoexcited molecule to yield a radical pair (Equation 7), whilst the second involves an intermolecular hydrogen abstraction reaction between excited photosensitiser and hydrogen donor (Equations 8 and 9).
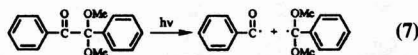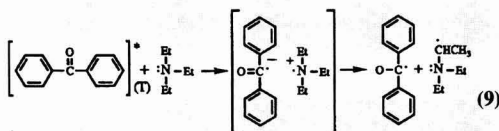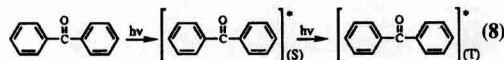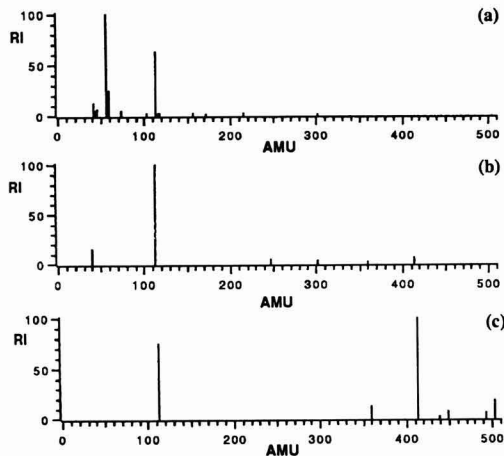
In Equation 7, 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba Geigy) is used as representative photoinitiator whilst the triethylamine benzophenone complex is used as a photoinitiator system where hydrogen abstraction from the amine, by the triplet excited ketone, is observed. Technically any amine can be used for this process with tertiary amines being the most efficient. Prepolymer mixtures containing monomers which preferentially quench the excited triplet state of benzophenone do not polymerize quickly enough for curing processes, thus, in such systems, the free radical type photoinitiators are preferred. In terms of chemical kinetics, UV curing reactions which are initiated by

free radical photoinitiators follow a typical chain reaction pathway. The kinetics of such processes is given by Equation 10[11-13].

$$R_p = k_p/k_t^{0.5} \, (I_o \, \phi \, \epsilon[S] \, I)^{0.5} \, [M] \qquad (10)$$

where I_o is the intensity of the incident light, ϕ is the quantum yield for radical production, ϵ is the molar extinction co-efficient of the photoinitiator at the wavelength of UV employed, S the initiator concentration and I the pathlength of light through the sample. At higher initiator concentrations deviations from the square root dependence have been observed14 and at concentrations higher than l millimolar rate of initiation follows Equation 11.

$$R_i = \phi \, I_o \, (1 - e^{-\epsilon[S] \, I}) \qquad (11)$$

UV Systems – Cationic A recent development with UV photoinitiators is the use of cationic materials[15-16]. Typical examples of such photoinitiators are triarylsulfonium salts, beta-ketosulfones, aryldiazonium salts and diaryliodonium salts, the most commercially significant of these to this time being the triarylsulfonium salts. In these cationic systems, the sequence of activation steps is similar to free radical polymerisation, i.e. photoabsorption, sensitisation, initiation, propagation and finally termination. The termination process is however slow and is responsible for the well recognised dark cure phenomenon. The effect of UV is to split the photoinitiator into a cation radical and a free radical fragment. Typical mechanisms[17] for these processes are shown in Equations 12-14 (triarylsulfonium salt) and Equations 15-18 (iodonium salt in ring opening polymerisation).
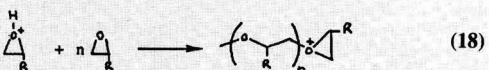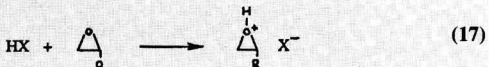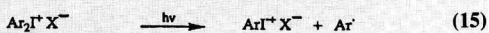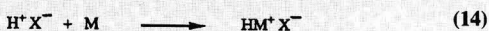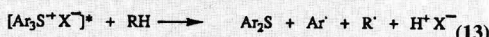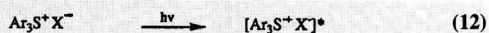
$$Ar_3S^+X^- \xrightarrow{h\nu} [Ar_3S^+X^-]^* \qquad (12)$$

$$[Ar_3S^+X^-]^* + RH \longrightarrow Ar_2S + Ar^{\cdot} + R^{\cdot} + H^+X^- \qquad (13)$$

$$H^+X^- + M \longrightarrow HM^+X^- \qquad (14)$$

$$Ar_2I^+X^- \xrightarrow{h\nu} ArI^+X^- + Ar^{\cdot} \qquad (15)$$

$$ArI^+X^- + RH \longrightarrow ArI + R^{\cdot} + H^+X^- \qquad (16)$$

$$(17)$$

$$(18)$$

Cationic systems are not subject to oxygen inhibition, but are quite sensitive to nucleophilic impurities, such as water, which can neutralise the cationic sites and terminate propagating chains. The complex metal halide anions of the onium salt initiators therefore must have a special combination of low nucleophilicity and ability to form strong acids on decomposition. Rates of polymerisation are dependent on the acids derived from the anion, the order of reactivity for common anions is as follows $SbF^{-6} > AsF^{-6} > PF^{-6} > BF^{-4}$. Reactive monomers or oligomers currently used have been reported at recent RadTech meetings, particularly RadTech 1990 and include cycloaliphatic epoxide, glycidyl ethers, vinyl ethers or epoxysilicones. Hybrid systems which utilise the radical produced by the onium salts are also important. Thus acrylate/vinyl ether and epoxide/acrylate combinations have been demonstrated to cure successfully. Maleate/vinyl ether combinations have also been reported as well as hydroxyl functional oligomers which participate in epoxide ring opening reactions. Some onium salts have limited solubility in the current range of reactive diluents, however, alkoxysubstitution of diaryliodonium salts have been found to produce better solubility, lower toxicity, higher reactivity and susceptibility to photosensitisation. Novel aromatic sensitisers and salts have also been found to enhance polymerisation in these processes[18-19].

Applications

The UV/EB technology possesses a number of advantages which are reflected in the range of applications currently being used. The advantages and disadvantages in the use of radiation curing techniques have been frequently listed in the literature and are summarised in Table 2. Two of these advantages are of particular importance. Thus the environ-

Table 2
Advantages and limitations of UV/EB curing

Advantages	Limitations
solvent free	higher cost of materials
low energy consumption	line of sight curing
low temperature requirements	UV-photon penetration
small space requirements	high cost of equipment (EB only)
rapid dry	skin irritation/sensitisation
totally controllable reaction	no FDA approval
advantageous physical properties	
higher productivity	
less wastage	
novel products	

mental problems associated with solvent emissions favour processes that are solvent free and the rising oil prices due to the current international crisis are likely to cause companies to seek processes where energy costs involved in routine running are significantly reduced. It will be recalled that the first energy crisis in the early seventies led to rapid expansion in energy saving processes such as UV. In this respect the cycle may now be repeating itself. A comprehensive list of representative applications of UV/EB curing systems is presented in Table 3. Of this group, the printing and graphic arts industry has been one of the first to adopt the UV/EB curing technology widely as a viable solution to the problems

Table 3
Applications of UV/EB curing

Timber filler	Galvanised metal tubing
Photopolymer print plates	Fibre optic coatings
Photoresists	Clear hard coats
Large scale integrated circuits	Metallised plastic coatings
Floor tile coating	Adhesives
Offset inks	Flat wood finishing
Overprint coatings	Silicone release coatings
Dental bonding	Electrical encapsulation
Screen print inks and coatings	Optical discs
Narrow web printing	Plastic tube coating
Vinyl and paper laminates	Plastic bottle coating
Vinyl flooring	Solar reflective films
Metal decorating	Abrasive binders
Metal and plastic name plates	

of solvent emissions and low cure speeds. UV cured inks and varnishes are now used in many large printing establishments for application to almost every type of substrate from paper to plastic to metals. The timber industry also has for a long time been using radiation curing on flat panels to produce scuff, solvent and stain resistant high gloss coatings. Although a late starter, the electronics industry has now adopted the UV/EB technology, particularly utilising the advantages of solvent-free rapid curing for sensitive components and production-line processing.

Cellulosic substrates

Paper and board

In the area of graphic arts, the initial attraction of radiation curing, particularly UV, for printers was the excellent gloss and rapid drying characteristics of both inks and varnishes. Many of the other unique properties of UV coatings such as scuff and solvent resistance have subsequently been utilised to advantage in a variety of printing applications. The slow acceptance by the printing industry of UV/EB curing in the formative years has now largely been overcome by the excellent track record of the technology. Early concern about possible skin irritancy of the coatings and UV exposure hazards have been surmounted with better chemistry and better shielding techniques. Table 4 summarises the range of coatings currently offered by various suppliers. These are available for application via roller coater, gravure, screen flexographic, lithographic or letterpress print methods.

Table 4
Current commercial coatings for printing and packaging

Coating Type	Application
Varnish	matt
	gloss
	gluable
	foil stamping
	abrasion resistant
	acid resistant
	solvent resistant
	stain resistant
	water and freeze resistant
	food products (indirect contact)
	high slip
Inks	process and PMS colours
	fluorescent
	"scratch off"
	"invisible"
Release Coatings	tight release
	easy release
	controlled release
	differential release
Adhesives	laminating
	pressure sensitive
	reverse
	piggy back
	desensitisers

Coating formulators have responded to the needs of the printers by expanding the range of coatings offered to satisfy requirements for faster cure speeds (or fewer lamps), in-line wet on wet over conventional inks and new printing substrates. Equipment manufacturers have contributed to the technology with innovations such as higher intensity lamps, cooler operation, interdeck curing, doped lamps for specific curing requirements, instantaneous on-off and special

geometries to reduce gripper shadow cure problems. In addition to printing, radiation curing has also been applied to the fields of adhesion primers, release coatings, adhesives and adhesive desensitisers.

Wood

The increasingly stringent restrictions on the use of volatile organic compounds is placing strong pressure on the wood finishing industry to remove solvents from their operations. For flat panel processing, UV or EB is becoming one of the favoured alternatives. With respect to UV, the first major application in wood curing involved polyester/styrene coatings twenty years ago. Since then the application of UV curing to wood has grown considerably. With the increase in line speeds to >20 metres/minute, the use of acrylate chemistry has become more prevalent even though it is more expensive. However, with acrylates, general cure performance is better and lower film thicknesses are capable of being achieved for a given level of performance.

Typical wood coatings used include:
* Reverse roll coat fillers (paste filler for chipboard, 60-100 gsm)
* Forward roll coat sealers (low viscosity for wood, wood veneer or hardboard, 25 gsm)
* Curtain topcoat (for wood, wood veneer, 200-300 gsm for polyester, 70-200 gsm for acrylates)
* Roll coat topcoat (for wood, open grain, 10 gsm, gloss or matt).

With respect to EB curing on wood, the technology has been particularly successful in large scale timber processing, lines having been established in the US, Europe and Japan. Two US operations use EB to bond woodgrain paper impregnates to the substrate via a timber filler/laminating adhesive. The adhesive is applied and pre-gelled using UV to create cohesive tack, the paper impregnated in line and laminated. A tie coat and finally one or two curtain coats are then applied and all coatings EB cured simultaneously at speeds up to 50 m/minute. This is illustrated schematically in Figure 2. The products produced by EB are superior in all respects to low pressure melamine laminates and have equivalent properties to high pressure laminates except in respect of wear resistance. A comparison of the properties of low pressure laminates with EB cured panels is shown in Table 5.

The most recent radiation curing developments in the wood finishing industry involve 3-D processing. Equipment is now available to satisfactorily cure large objects with difficult geometries. Using a combination of specialised lamps and coatings it is possible to finish wood surfaces with a high gloss, pigmented and opaque "wet-look" appearance.

Electronics

UV/EB curing is expanding rapidly in the electronics industry. Commercial applications include
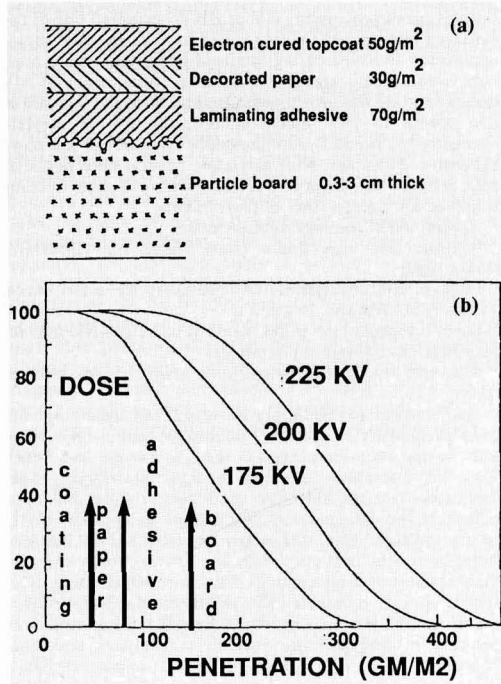* photoresists
* through-hole plugs for PC boards
* photoimageable solder masks
* conformation coatings
* encapsulants and potting compounds.

Metal

Metal surfaces are routinely coated using UV cured inks and varnishes for metal decorative purposes. Because of the high shrinkage and generally poor adhesion of acrylate coatings to metals, a solvent based primer coat is usually

employed as the primary coating. More recent advances in acrylate chemistry have yielded coatings which can be used in direct contact with metals in all but the most demanding of applications (formability).

Figure 2

EB laminating process for paper: (a) Typical section, (b) Processor penetration performance

(a)

Electron cured topcoat 50g/m^2

Decorated paper   30g/m^2

Laminating adhesive   70g/m^2

Particle board   0.3-3 cm thick

(b)

DOSE

225 KV

200 KV

175 KV

coating   adhesive   board

paper

PENETRATION (GM/M2)

Metallised papers and foils are being produced by EB techniques[20,21] and are designed for a variety of decorative and functional purposes including label stock and microwave packaging. A schematic of the EB section of the process is seen in Figure 3. UV is also being used for the production of these materials.

Coil coating by radiation curing is currently limited to EB finishing and adhesives for film laminations as well as anticorrosive primer coats. Much current research is being performed with UV cationically cured materials on metals. Such systems possess the potential to solve problems hitherto unachievable with free radical processes. In particular, the properties of low irritancy, fast cure response, shadow zone curing and low shrinkage on substrates such as metals and glass are capable of being solved with cationic chemistry.

Plastics

The use of plastics as printing substrates and as part of laminates in labels for graphic arts applications is increasing

Figure 3

EB curing of films – Electrocurtain® Processor

LINEAR CATHODE

BEAM CONTROL ASSEMBLY

FROM POWER SUPPLY

CURED MATERIALS EXIT

FOIL WINDOW (ANODE)

ELECTRON CURTAIN

ACCELERATING AND TREATMENT ZONE SHIELDING

COATED OR LAMINATED WEBS (Paper, Cardboard, Plastic Film, Metal Foil etc)
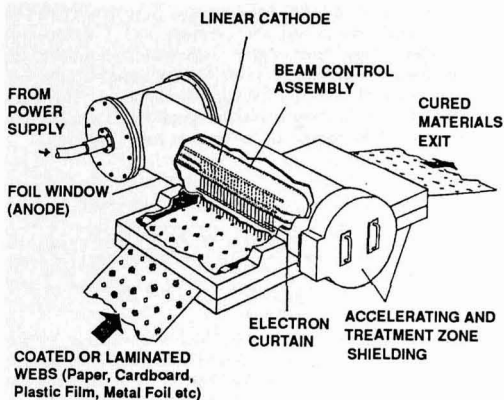
Table 5

Comparison between low pressure melamine laminate and uniface electron beam cured panels.

Test	Unit	Low Pressure Performance Limits[a]	Test Values[b]
Hoffman scratch resistance	grams	400[c]	1200
wear resistance LD3-3.01	cycles to failure	100	145
Impact resistance LD−3.03	inches	15	24
Boiling water resistance LD3-3.05	20 minutes	slight effect	no effect
High and low temperature resistance LD3-3.06	20 minutes	slight effect	no effect
Stain resistance LD3-3.09	reagents 1-23[d]	no effect	no effect
	reagent 22	no effect	moderate effect
	reagents 2429	moderate effect	no effect
Cigarette resistance LD3.1 1	rating	moderate effect	moderate effect

[a] For melamine laminates.
[b] Test values, obtained by PPG (Pittsburg Plate Glass) Laboratory on EB panels.
[c] Test panels, no performance available.
[d] Stain resistant test reagents from NEMA Standards LD.

rapidly. Substrates commonly used include PVC, polypropylene and polyethylene. UV inks, varnishes and adhesives are ideal for these non-porous substrates. Modification of surface properties by radiation grafting/curing processes is also topical[22]. Thus the grafting of methacrylic acid to PVC, has been used to improve salt spray resistance of PVC precoated steel[23]. In addition the grafting of acrylic acid on polyethylene has been reported as a commercial process[24].

Glass

The use of primary and secondary coatings for optical fibres is well accepted technology. Inks and varnishes are readily available for screen printing to glass bottles. More recently, UV coatings have been proposed for application in glass laminates and to reduce the weight of glass bottles.

Miscellaneous applications with special substrates

A number of novel miscellaneous UV/EB systems have recentl become commercialised. Thus the mono-web label making process (Figure 4) illustrates the use of UV to cure a silicone which is directly applied to the ink printed on a plastic support. This allows the label to be rewound without the use of a throw-away silicone backing sheet. Current developments in this area are designed to achieve UV curing with the pressure sensitive adhesive also. Other processes involving special substrates include EB static dissipative coatings for protection of electronic components[25] and UV coated polycarbonate for touch panel overlays[26]. In addition UV/EB curing is being applied to binders for magnetic media, 3-dimensional modelling (stereolithography), pressure sensitive adhesives, textile and leather coatings, staple cements, composites, sealers for fibre reinforced plastics and microencapsulation.

Figure 4
Mono-web label process

Release Layer

Print Substrate

Adhesive
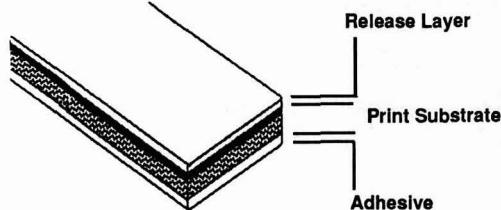
Equipment

With UV, the development of equipment for printing continues to be an important area. Most new printing presses (for sheet fed lithography) have provision for integration of UV as part of a multimode drying unit in combination with infrared/hot air, permitting the printer to adopt a variety of coating systems according to commercial needs.

The application of UV to screen printing has received much attention, particularly, the development of UV rotary screen printing equipment. This continuous curing system is achieved through the use of a seamless rotary nickel screen, which is engraved in the same way as a flat-bed screen. The problem of drying in the screen is virtually eliminated by the use of radiation curable coatings. The quality of such systems is now as good as flat-bed screen printing.

The release of microwave powered 600 W per inch lamps

represents a major advance in UV curing technology[27]. A schematic of the new lamp system is presented in Figure 5. In addition to the economic benefits of having fewer lamps to achieve the same radiation dose, the potential for higher line speeds is also obvious. Cure efficiencies have been found to be increased by a factor >2 for acrylate systems and >S for cationic epoxies in changing from 300 to 600 W/inch lamp systems.

Figure 5
6 kW Electrodeless lamp
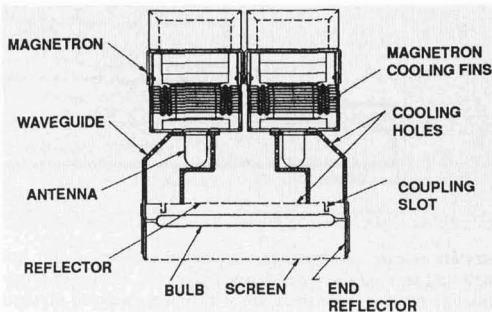
EB technology continues to advance with the acceptance by industry of the ESI curtain-type electron processor[28] and subsequent improvements. One particular attribute of this technique is the ability to cure multiple ink films and varnish in-line wet on wet. The system has no limitation on film weight (up to 150 microns approx.), pigment choice or opacity. A more recent development with great potential in the area of narrow reel web application is the invention of the WIP EB processor by RPC Industries (Figure 6). This technique provides the label printer with a cold cure system which is capable of totally reliable wet on wet curing at line speeds in excess of 400 m/minute. In addition, the degree of cure is more carefully controlled and film residuals are virtually negligible.

Future trends

A variety of applications in widely differing fields are currently being explored for utilisation of UV/EB technology. The following areas are amongst those being examined in detail at the present time.

Upgrading of paper and other substrates

Many chrome-coated and clay-coated print stocks will in the future be manufactured utilising EB or UV curing processes. Such coatings are ideally suited to UV inks and varnishes, but currently do not print well using oil based inks. Such stocks may be designed with such high gloss levels that UV varnish may no longer be required.

Adhesion to metals and metal foils has been a continuing problem for UV cured coatings. The use of primers and/or thermal "post cure" is currently employed to reduce the magnitude of the problem which results from the significant shrinkage of these coatings. More recently, developments in alternative curing mechanisms indicate that coatings with excellent adhesion to metals and other nonreactive substrates will soon become commercially available.

Lamination of films (adhesives)

Release coatings The current generation of UV silicone

Figure 6
WIP Processor system: (a) Overview of WIP components, (b) WIP Electron gun typical uniformity

(a)

(b)
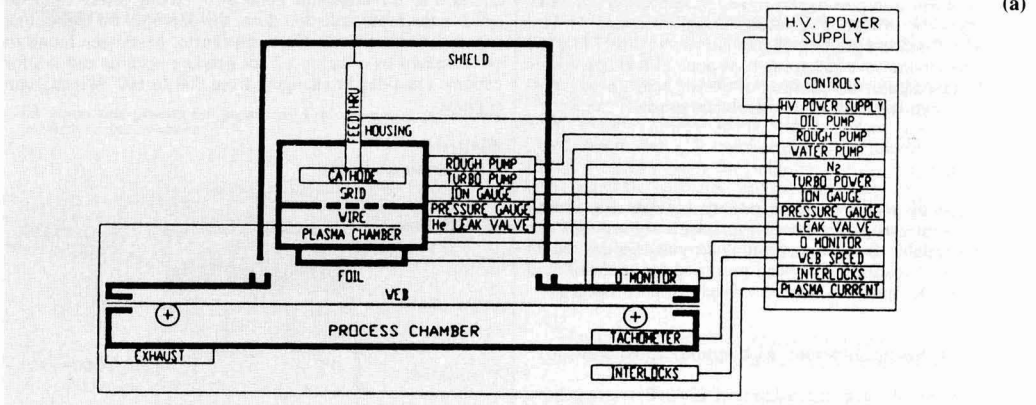
acrylate release coatings are reasonably satisfactory for hot melt and non-acrylic water-borne adhesives. However cross-linking, reactive adhesives are a problem because of their attack on residual acrylates in the silicone release coating. This difficulty occurs particularly when the acrylic adhesive is applied and dried in contact with the release liner. Recent developments with cationically cured silicone-epoxides have overcome many of these problems.

Pressure sensitive adhesives The development of EB curable pressure sensitive adhesives has been slow. The types of polymers required to achieve these properties are not readily synthesised and more work needs to be performed in this important field, particularly to eliminate odour and irritancy problems.

Laminating adhesives UV cured laminating adhesives are available for cellulose-polyolefin or polyolefin-polyolefin laminating. The critical requirement is that one substrate be transparent to UV light. It is anticipated that in the future these coatings will be extended in application to a wider range of substrates and/or substantially higher peel strength requirements.
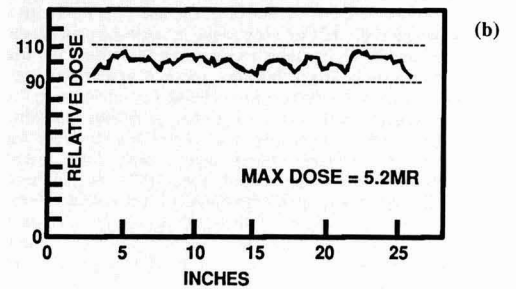
Miscellaneous developments

This area includes the development of barrier coatings, the use of UV/EB to replace extrusion processes, security coatings, conductive coatings and the formulation of novel membranes.

In the equipment field, increasing interest is being shown in the application of excimer lasers to curing of coatings. Currently the equipment needs further refinement, however when this is achieved one of the interesting features of the technology is the potential for one laser light source to be "piped" to a number of locations (e.g. interdeck) using optical fibres. In addition the process offers faster speeds than mercury vapour sources and new possibilities for the curing of heavily pigmented systems.

Conclusions

Extensive work over the past twenty years in UV/EB curing has brought the technology to a degree of sophistication where it now complements the other accepted surface coating processes. Overall market penetration of the technology is still relatively small, however the potential to develop not only new products but also unique methods for improving traditional processes remains. The growing import of environmental issues together with the current potential energy crisis means that the UV/EB curing technology will maintain strong growth, limited in many ways by the ability of research workers to develop not only appropriate new chemistry but also higher performance curing equipment.

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DECEMBER JOCCA
WEATHERING

Physics of high film build cathodic electrocoatings

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Introduction

Electrodeposition, a process by which charged paint particles deposit onto an oppositely charged electrode forming a uniform organic film, is considered to be the most significant materials and processing development in the recent history of industrial painting. The rapid progression of polymer and formulation chemistries and processes (Table 1) has enabled a continual evolution and advancement of technology from introductory anodic systems in the early 1960s to the actual cathodic electrodeposition coatings[1-7]. Success of electrodeposition coatings is not only due to the physical performance and process benefits, but also due to potential additional advantages including opportunities for high levels of automation, high levels of materials utilization efficiency and reductions in organic solvent emissions[8,9].

Table 1

History of electrodeposition technology in automotive industry

	Technology	Chemistry	Film Thickness
1964-1972	anodic	maleinized natural oils	0.025mm
1972-1976	anodic	maleinized polybutadiene	0.025mm
1976-1984	cathodic	epoxy-amine	0.018mm
1984-today	cathodic	epoxy-amine	0.025mm and 0.035mm

The advancements in the development of electrodeposition coatings have generally been associated with automotive primers. The first technologies commercialized in 1964 were based on anodic processes utilizing carboxyl functional resins[1,10]. Film thicknesses were applied between 0.02 and 0.03mm. Cationic resins were introduced to the market in 1976 designed for better corrosion protection and increased throwing power for coverage of inner areas of complex parts. Film thickness with those systems was approximately 0.018mm[4].

Increased environmental demands encouraged the development of electrocoat materials providing higher film thickness capability, thus allowing a greater participation of electrocoat in the total painting process of automobile and other industrial products. This could allow a net decrease in solvent emissions from the total painting process.

This easily can be seen by comparing the contribution to emission of all paint systems used in automotive OEM business. Figure 1 shows data for solvent emissions in g/m² painted area. The highest value is reached by low solid basecoats and the lowest value by electrocoatings. Initial high film build developments utilized a concept of reverse painting processing. As a prototype process a powder[11] or solvent-borne primer was applied outside the part by spray application, then as a second step inner areas were coated by electrodeposition paintings. It was considered to be a remarkable step forward when replacement of the spray application electropowder coating which is called EPC was introduced[12-14].

For this technology fine powder particles of less than 0.005mm particle size were dispersed in a cathodic binder similar to the dispersion of pigment particles. Film thickness levels of more than 0.05mm easily could be attained without throwing power. This type of dispersion however had a significant tendency for settling because of problems related to powder particle wetting, particle size and particle size distribution. So the commercial success was limited[15].

Figure 1

Typical solvent emission data of electrodeposition coatings, primer surfacers and topcoats per m² coated area in automotive industry
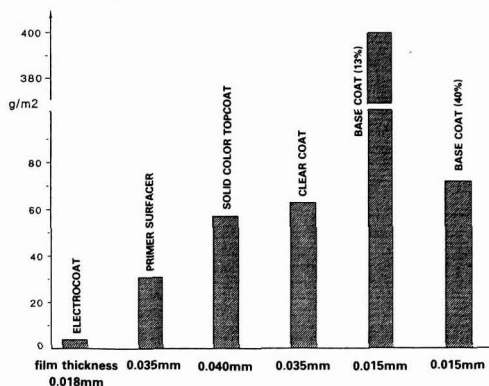
There were some other attempts to get film builds higher than 0.03mm by electrodeposition process, but they also were not successful even the dynamic behaviour of these systems achieving film thickness of 0.1mm in less than 30 seconds was of great interest[16-22].

A better chance for commercialization could be expected by such electrocoatings which could be used as a single primer in the standard coating lines with high film build characteristics. Those primers are today successfully commercialized[5].

This survey demonstrates that there are a lot of different ways to formulate high film build electrocoatings and that there is a high complexity of effects on the film build physics of electrocoatings. The target of this paper is to contribute to some important aspects of resin chemistry and its relation to film build of cathodic electrocoatings.

Application parameters

The primary influencing factors for the deposition behaviour of electrocoatings under potentiostatic conditions are voltage, time specific bath conductivity, solids content, solvent content and bath temperature. These are the key factors which are focused on in research and development programs directed towards optimization of application parameters for a given electrocoat system. Early potentiostatic experiments clearly defined the relationship of voltage and time to film deposition[2,23,24].

In general an increase in voltage and/or deposition time positively influences the deposited film thickness as shown in Figure 2.

Figure 2

Film thickness-voltage characteristics for potentiostatic experiments[23]
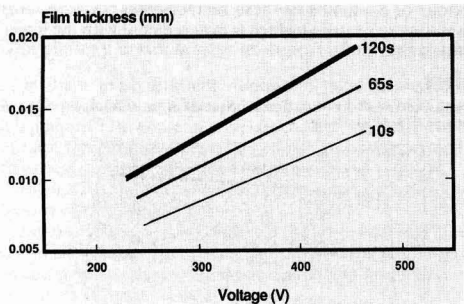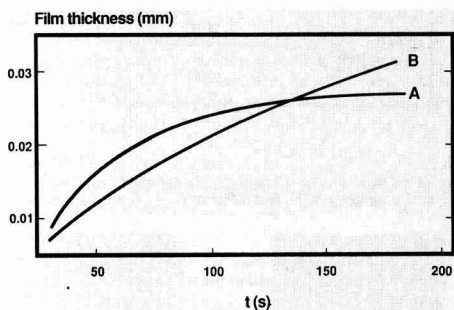

Film thickness (mm) vs Voltage (V)

Figure 3 shows for two different electrocoat Systems A and B that film thickness increase over time is specific for each electrocoat formulation.

Figure 3

Relation of film thickness to deposition time for different electrocoatings[23]

Film thickness (mm) vs t (s)

Both factors, time and voltage have technical limitations. Voltage cannot be arbitrarily increased for a given system because film disturbance will occur when a certain voltage, the so-called "rupture voltage", has been reached. In other systems it was found that high voltage can decrease film thickness[21].

Likewise, deposition time cannot be excessively extended for economic reasons. In addition certain systems attain such high levels of deposited film resistivity that longer deposition times have little beneficial effect on film thickness (see Figure 3, System A).

Influence of bath temperature on the film thickness-experimental section

Specific bath conductivity mainly contributes to throwing power of electrocoatings rather than to film thickness[24].

The solvent concentration and solids content plays a more important role than bath conductivity. Investigations with unpigmented resin solutions demonstrated the positive influence on film thickness with increasing resin concentration (Figure 4). Nevertheless high solids contents of electrocoatings also have limitations in practice due to increased instability. This may be detected first in ultrafiltration costs in terms of low flux stability. Because of all these limitation to process parameters or paint formulation it is clear that high film build cathodic electrocoatings were completely new designed paints.

Figure 4

Effect of voltage on the film thickness and resin concentration[26]

Film thickness (mm) vs Resin (%)
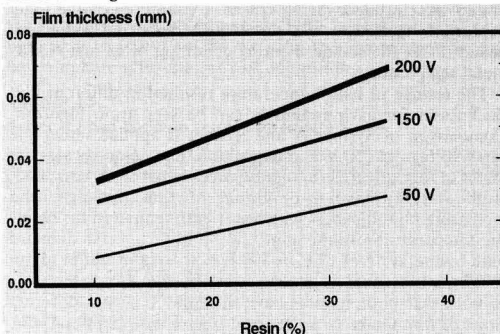
The influence of bath temperature seemed to be most interesting for better understanding how to design resin chemistry and/or paint formulations for high film build electrocoatings. Increasing the bath temperature above room temperature results in higher film build for some cathodic electrocoating systems as was reported by Miskovic-Stankovic[26]. For two applied voltages the described system has a minimum, below that film thickness again increases (see Figure 5).

Figure 5

Film thickness/bath temperature relationships for standard cathodic electrocoating systems[26]

Film thickness (mm) vs T (k)
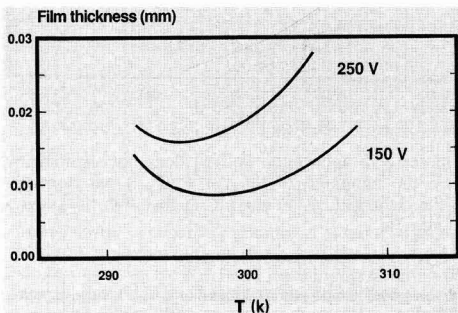
For the studies described in the following sections two different standard cathodic electrocoatings were used based on epoxy resin backbones and isocyanate crosslinkers. The standard temperature of these electrocoatings is between 27°C up to 30°C. Film thickness of 0.02mm for System A and 0.035mm for System B could be obtained by voltages between 250 and 400 V and deposition time of 2 min. Bath datas like pH, specific conductivity, P/B-ratio and solids content were kept constant (Table 2).

Table 2

Physical datas of investigated cathodic electrocoatings

|	System A	System B
pH	6.1	6.1
Solid Content[1]	18%	18%
P/B[2]	0.3	0.3
$\varkappa_L$ (20°C)[3]	1.1 mS/cm	1.3 mS/cm
Rupture Voltage	420 V	400 V

[1] 30 min./180°C
[2] pigment to binder ratio
[3] Specific conductivity of paint

The electrocoatings were applied on a 10×20cm phosphated panel in a 5 1 tank where a graphite stick was placed at a distance of 15 cm as a counterelectrode. The deposited electrocoat was rinsed with deionized water and baked under the standard curing condition of 15 min./185°C metal temperature.

The change of bath temperature resulted in different film thicknesses for each system as can be seen from Figure 6. Comparison of System A and System B applied under the same voltage of 250 V and deposition time demonstrates the effect of film thickness and differences between 20 and 30°C. Both systems have a minimum of film thickness and increasing film thickness with lower bath temperatures below the temperature of minimum film build (T_{min}). At standard bath temperature of 27°C or 300 K both systems differ about 0.017mm film build as was described earlier. It is interesting to note that both systems have different T_{min} and different slope of film thickness increase at higher bath temperatures.

Figure 6

Comparison of film thickness of two dispersions at different bath temperatures with the same voltage and deposition time
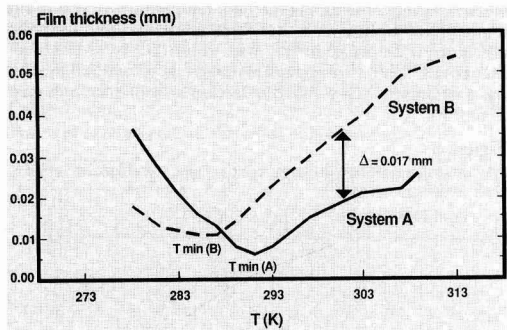
An increase in application voltage does not significantly influence the minimum of the curve (T_{min}) but normally moves the right half of the curve to higher film thicknesses (see Figure 7).

Figure 7

Film thickness/bath temperature relationship at two voltages applied for system A

A, B, C = REM - Pictures of deposited film
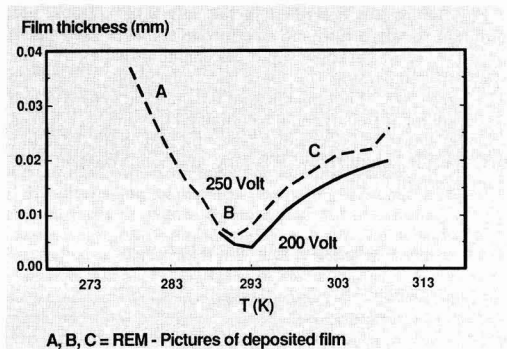
Next the electrical data of paint A at different characteristic points of bath temperature, were examined.

The plots of resistance and coulombs (Figures 8 and 9) versus deposition time at different bath temperatures under the same geometrical conditions confirmed the film thickness development. So at 12°C or 285 K and 28°C or 301 K roughly

the same coulombs at the end of deposition have to be observed which give the same amount of deposited film or the same film thickness. A difference can be seen in the dynamic behaviour of coulombs at these temperatures. At 20°C less coulombs were recorded which is in agreement with the lower film thickness.

Figure 8

Coulombs versus deposition time of System A (a = total, b = first 5 seconds of deposition time)

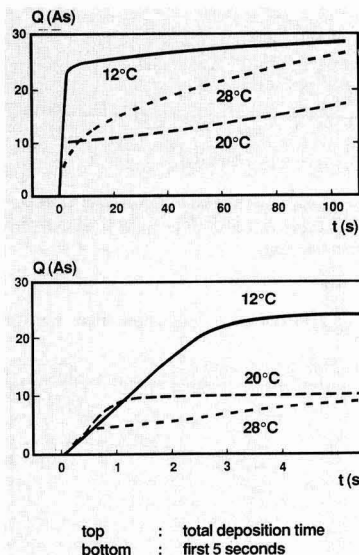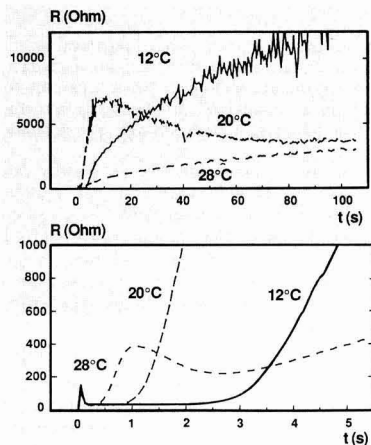top : total deposition time
bottom : first 5 seconds

Figure 9

Resistance versus deposition time of System A (top = total; bottom = first 5 seconds of deposition time)

A careful look at the first 5 sec. of the deposition process showed that differences in coulombic consumption have occured in the first second of deposition process.

Further information can be seen from the resistance versus bath temperature plots of the same experiment. The upper plot as well as the lower expanded plot clearly shows that there is a completely different deposition mechanism at different bath temperatures. The resistivity of the film at 12°C

bath temperature increases slowly, while at 28°C bath temperature it increases rather quickly but then keeps the film to a slow resistance build up. At 20°C the film resistivity again behaves completely differently.

Morphology and viscosity of deposited electrocoatings

If there exist different deposition mechanisms the film morphology also could be expected to be different. Figure 10 a-c demonstrate non-cured electrocoated films, electrocoated at bath temperatures near T_{min} of the above mentioned film thickness versus temperatures curve.

Figure 10a demonstrates the phosphated substrate surface before electrodeposition

Figure 10b is a photomicrograph by scanning electron microscopy taken after a very short deposition time: there has coagulated around the burst gas blisters. The structure of the phosphated panel can still be seen.

Figure 10c is the wet electrocoat surface after deposition for 2 minutes. The electrocoat film shows a filigree structure with many areas that have not been coated and the substrate can be clearly seen.

Figures 10d-f are SEM-pictures of, after 2 minutes deposition time, non-cured electrocoat films at 280, 290 and 300 K.

Figure 10d, left branch of the film thickness versus temperature curve, demonstrates a very brittle surface with a lot of holes.

Figure 10e, minimum of the film thickness versus temperature curve corresponds exactly to Figure 10c.

On Figure 10f, right branch of the curve, electrocoat structure of Figure 11e has melted to small lakes with small conductivity canals at the base.

Figure 10

SEM pictures of wet film surfaces of System A deposited at different bath temperatures, (voltage = 250 V), and deposition time at 18°C.
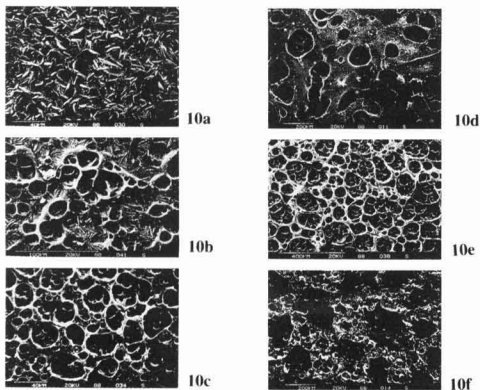
These and other typical photomicrographs of freshly deposited and the uncured electrocoat films give the same fundamental information.

First: The structure of the dispersion particles is after deposition completely destroyed and not detectable.

Second: the wet film of the uncured film is never pore free, smooth or flat.

Third: With increasing bath temperature the film shows flow properties.

The visual impressions confirm different film build mechanisms at different bath temperatures for the same electrocoat material.

Depositions starts with separate material pots, which later build into a homogeneous film. With "hard dispersions" the porous structure keeps stable — with "soft dispersion" the structures melts together. With increasing bath temperature the structures become more soft. With "soft dispersion" and high bath temperature the wet film is homogeneous within half a minute after the start of deposition.

Figure 11
Schematic film thickness versus temperature profile
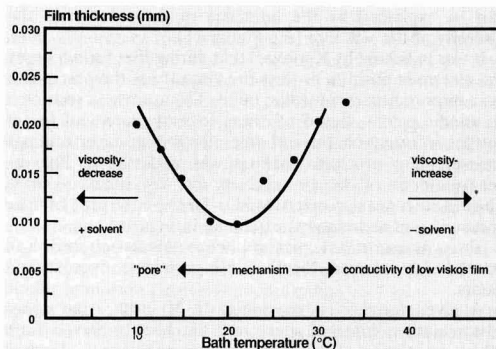

Hypothesis of the dependency of film thickness to bath temperatures.

Electrocoat coagulation is only possible if current flows. Therefore conductivity is necessary which is given by the conductivity of the bath. The electrocoat itself is non-conducting. Therefore during the total deposition time a certain conductivity must be given. The very porous structure of the wet film, shown in the photomicrographs by scanning electro microscopy is a precondition for current.

Both branches of the film thickness versus bath temperature curve (Figure 11) indicate two mechanisms of conductivity. We propose a "pore model" for the left branch, where gas blisters play an important role. Caused by relatively high viscosity the wet electrocoat film is stiff and does not melt. Gas blisters don't adhere at the wet film and thus electrical conductivity remains. Caused by high viscosity the film keeps open for a relatively long time during electrode position (see Figure 8). Later during deposition, when gas blisters can no longer disappear, resistance increases rapidly to normal values. With increasing temperature towards T_{min}, viscosity decreases.

Figure 12
Principle of Shear Rheometer for film viscosity measurements
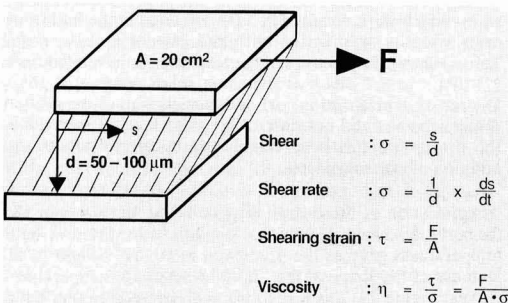
At T_{min} the mechanism of the process changes. The additional mechanism starting at T_{min} is an increase of conductivity by the higher temperature and lower viscosity. Probably electrolyte concentration in the wet film also

increases with lower viscosity and higher temperature.

It is well-known that resistance curves of electrocoat deposition include two processes which are separated and can be observed in the slope of the resistance versus temperature curve. Probably the first process is basically more a pore mechanism whereas the second process is more a "conductivity mechanism".

It is well-known that the addition of solvents significantly change deposition behaviour of electrocoats. This behaviour can be explained by the influence of the solvent on the viscosity of the wet film (see Figure 11).

It was indicated by Krylova[27] that during film formation by the electrode position process the viscosity of the precipitate is an important factor for film build. This study was restricted to anodic paints. Based on these investigations and to get further information for cathodic electrodeposition coatings measurement of electrocoatings was undertaken. For the measurement of wt (= viscosity of wet films) a stress rheometer was constructed. The principle of the measurement technique is explained in Figure 12.

Two plain metal pistons were electrocoated and immediately pressed together using weights over several hours.

A given force F (= maximum 10 N) pushes the upper piston until a constant shear rate has been achieved from which calculation of the shear viscosity analogue is obtained using the following formula.

$$wt = \frac{F}{A}$$

A is area of piston. The experiments are carried out for at least 10 hours until an equilibrium in the velocity has been reached. The small angle of σ also indicates that a very precise device is necessary, which has carefully to be constructed.

The measurements were carried out at constant temperature at 23°C and high relative humidity to avoid drying of the samples because water content influence could be considered as very sensitive to the effective viscosity.

In a first series we measured the viscosity of the deposited film of System A and B which were known as the standard film build and high film build system.

As expected the viscosity of the System A is 10 times higher than the viscosity of the System B. We also observed decreasing viscosity with increasing shear rate (Figure 13).

Figure 13

Viscosity of System A and System B after deposition
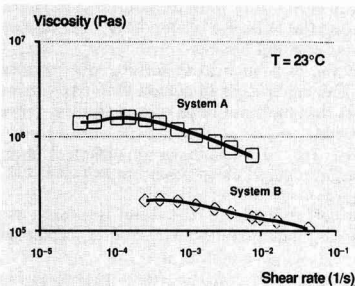
Model dispersions

At least the different described observations have been controlled by designing model-dispersions to study the influence of resin viscosity on the film build of electrocoatings.

Table 3

Datas from model dispersions in correlation to T_{min}

Resin			dispersion		T_{min}
	viscosity	solid cont.	pH	% neutralization	particle size	
C11/92	2.2 dPas	14.7%	8.3	40	110nm	10°C
C11/93	3.1 dPas	14.7%	8.4	40	100nm	17°C
C11/94	3.8 dPas	14.9%	8.4	40	100nm	24°C
C11/95	8.7 dPas	14.8%	8.5	40	80nm	31°C

Based on alkyl phenol modified amine terminated epoxy resins which were mixed with TDI crosslinkers the backbone resin viscosity was varied with the phenol/epoxide ratio. Table 3 shows the viscosity of the resulting resins ranged from 2.2 dPa s to 8.7 dPa s at the same solids content of 15%. Degree of neutralization, pH and particle size of the related dispersions also did not differ. The same level of solvents in the dispersions has been established by ultrafiltration and addition of phenoxypropanol.

Application of those resin dispersions at 200 V under the formerly described geometrical conditions at different bath temperatures gave us the T_{min}-point at 10, 17, 24 and 31°C. Because of the shape of the film thickness/bath temperature-curves (Figure 14) this is identical with decreasing film build at standard (27°C) temperature conditions. An exception is resin C11/95 with T_{min} of the related dispersion at 31°C because for this dispersion there is higher film build at 27°C bath temperature. This is why one is then below T_{min} where film thickness also increases.

Overall these experiments confirm, that there is a strong link between resin viscosity of a given resin chemistry and the film build under standard application conditions.

Figure 14

Film thickness versus bath temperature plots of model dispersions
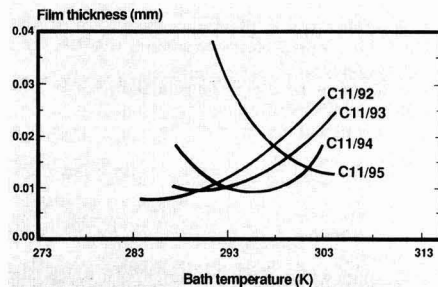
A process for encapsulating inorganic pigment with polymeric materials

by R. L. Templeton-Knight, Tioxide Group PLC, Central Laboratories, Portrack Lane, Stockton-on-Tees, Cleveland.

Abstract

A new method of encapsulating TiO_2 pigment with a uniform polymer coating is described. The procedure follows the emulsion polymerisation of methyl methacrylate using ultrasonic vibrations during part of the reaction.

Transmission electron micrographs show that ultrasound enhances the polymerisation process and increases the degree of encapsulation of the product.

Various modifications made to the initial system indicated that pre-treatment of the pigment prior to polymerisation resulted in a more uniform polymer coating. In addition seed and feed addition of monomer to the mixture together with a single addition of redox initiators also gave a uniform polymer coating, at high coverage. The reaction using redox initiators appeared to proceed more rapidly than when using radical initiation.

Further research is likely to involve the use of monomers such as styrene and butyl acrylate as alternatives to methyl methacrylate.

Introduction

The development of novel types of inorganic particulate materials, e.g. pigments, is an active and important area of both academic and industrial research[1-5]. An area of this type of research which has seen much activity is that of inorganic powders coated with an organic polymer layer[6-8]. There are many perceived benefits from such a product, and some of these are listed below:

▷ improved particle dispersion
▷ better colloidal stability/resistance to flocculation
▷ improved compatibility with the dispersion medium
▷ enhanced (or at least less detrimental) properties

In particular, for the case of an opacifying pigment such as titanium dioxide which finds application in a number of consumer products, such as paints, plastics, inks, paper, etc.[9], the encapsulation of the pigment can offer advantages such as:

▷ improved opacity (all products)
▷ better dispersion (plastics)
▷ reduced flocculation (emulsion paints)
▷ less effect on mechanical properties (plastics, composites)
▷ less abrasivity (inks)

These benefits can be typified by the following example:

Emulsion paints

The introduction of water-based (emulsion) paints in the 1950's represented a major step towards producing environmentally friendly paint systems. Without doubt, the current macro-political trend towards environmentally acceptable products will lead to an increase in the use of water-based paints. However, there is a cost associated with the use of water-based paints, namely, that the utilisation of the opacifying pigment (titanium dioxide) is often reduced by the flocculation of the pigment particles in aqueous systems.

The opacity or hiding power of a latex paint depends on a) light absorption and b) light scattering, the latter being of most importance for white pigments. The hiding power depends mainly on the scattering effectiveness of the dispersed pigment particles, which in turn depends on the regularity and arrangement of particles in the film and on their particle size. If the pigments are uniformly spaced at an ideal distance, their light scattering power will be optimised as will the opacity of the film. However, if pigment agglomerates are present, the light scattering and the opacity will be reduced. Various attempts have been made to achieve an optimum physical disposition of pigments in a paint film, e.g. extender pigments, which act as mechanical spacers. However, flocculation occurs during coalescence of the binder (emulsion particles) upon drying.

Obviously, if a consistent polymer coating of uniform thickness could be applied to the surface of discrete pigment particles, then such an envelope of polymer could precisely determine the spacing between consecutive pigment particles in a paint film. For example, it has been shown by using a modification of the Kubelka-Munk theory[10] that the scattering power of pigment particles decreases as the pigmentation increases due to a crowding effect caused by the close proximity of the scattering centres, and that this effect can significantly reduce the cost effectiveness of the opacifying pigment.

The thickness of the polymer layer around the TiO_2 is primarily dependent on the pvc of the paint film. Pvc is the pigment volume concentration and is shown by the following equation.

$$pvc\% = \frac{\text{Volume of (pigment + extender)}}{\text{Volume of (pigment + extender + polymer solids)}} \times 100$$

Using the equation:

$$\left(\frac{d_1}{d_2}\right)^3 = \left(\frac{pvc}{0.55}\right)$$

Where d_1 = diameter of TiO_2 particles = 0.25μm
d_2 = polymer coating thickness

From this, it is possible to exactly determine the optimum spacing required between TiO_2 particles to achieve maximum light scattering, hence opacity, at the particular pvc of a paint film. Obviously it is not as simple as this and other factors are also involved.

There are other benefits in coating the titanium pigment with a continuous organic polymer layer; once encapsulated by a suitable polymer, the pigment is shielded from the effects of the atmosphere. This is an important area of concern for both producers and consumers of titanium dioxide pigment. The question of durability is important in that adverse durability properties of a pigment lead to product failure and customer dissatisfaction. Durability is the term given, in this context, to the photocatalysis reaction between titanium dioxide and organic polymers[11].

In addition, in paint preparation the effective dispersion of the pigment particles is an important process requirement. It is conceivable that an inorganic pigment with a polymer coating may have favourable dispersion characteristics.

With all these advantages, it is not surprising that many

attempts have been made to develop a technique to encapsulate pigment with a polymeric coating.

Our approach, at present, for encapsulating inorganic pigment with polymeric material, involves an emulsion polymerisation process. The monomer is usually ethylenically unsaturated, e.g. vinyl monomers including acidic monomers such as acrylic acid and esters of acid monomers such as methyl methacrylate.

Generally speaking, the process involves the preparation, initially, of a dispersion, usually aqueous, of the inorganic powder to be coated. Monomer is added to the dispersion and polymerisation is carried out by an appropriate technique. During at least part of the polymerisation the dispersion of the inorganic particles is subjected to ultrasonic vibrations which have advantageous effects which will be specified further in the paper.

Experimental

Materials

All materials were obtained from UK-based suppliers and were used as supplied without further purification. The major components were: TiO_2 pigment (TIOXIDE); methyl methacrylate (Aldrich); iso octylphenoxy polyethoxy ethanol (Triton-×-100 Aldrich); potassium persulphate and sodium metabisulphite (BDH); ethylene glycol dimethacrylate (Aldrich); aluminium nitrate (BDH) and methacrylic acid (Aldrich).

Apparatus

Standard emulsion polymerisation techniques were followed. A five necked, round bottomed, flask was heated by a water bath. The inlet ports of the flask were connected to an inert gas supply, a condenser and an inlet funnel. The central inlet port allowed the introduction of a stirrer paddle for agitation of the reaction mixture. At a later time an ultrasound probe was introduced through the fifth neck. A schematic diagram of the experimental apparatus is shown in Figure 1.

Figure 1
Pigment encapsulation apparatus
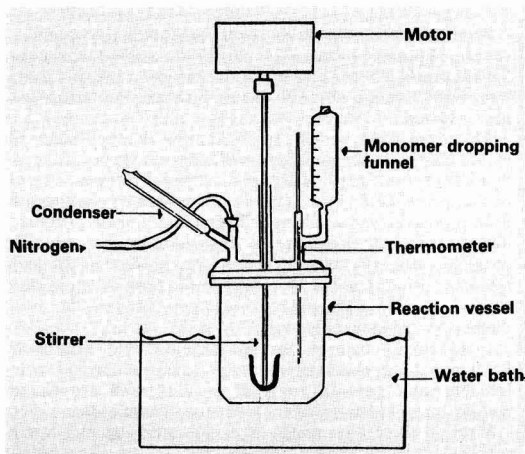
Method

General description

The inorganic powder used in our process was rutile titanium dioxide pigment obtained as reactor discharge in the vapour phase oxidation of titanium tetrachloride (chloride process).

Initially the titanium dioxide was formed into an aqueous dispersion, if necessary with the aid of dispersing agent. Usually, but not always, this dispersion was milled to break down any large agglomerates of pigment prior to the polymerisation.

A desired amount of this dispersion was then placed in the five-neck flask, the flask having been previously purged with an atmosphere of dry nitrogen, which was maintained throughout the reaction procedure. The slurry was mechanically stirred at 20°C for about 15 minutes.

Generally, at this stage, methacrylic acid was added to the dispersion, at 3% by weight on solids together with an aluminium salt at 4.5% by weight on solids. This addition serves to render the surface of the reactor discharge cationic. Aluminium nitrate was chosen as it has high cation charge density and it is relatively inexpensive. However, any multivalent cation can be used at acid pH, eg. Zn^{2+}, Ca^{2+}, Ba^{2+}, etc; for the purpose of this reaction it was beneficial to use a combination of a weak acid and a multivalent cation salt. This was agitated by stirring for about 15 minutes.

A cross linking agent was usually added to the dispersion at this stage, normally ethylene glycol dimethacrylate (EDMA), the amount added being in the range 10 to 50% by weight on monomer employed. At this point the temperature was increased to 40°C.

Potassium persulphate and sodium metabisulphite were used as redox initiators in the system, within a N_2 atmosphere. However, the polymerisation could also be conducted in air. The effect of the initiator concentration on the encapsulation process has been studied, and will be discussed later in this paper.

In the process, prior to mixing with the dispersion the monomer was formed into an aqueous emulsion using a nonionic or anionic surfactant to assist the emulsification. Normally, methyl methacrylate, in the range 2-25% by weight on inorganic solid was employed with Triton-X-100 as the surfactant. The polymerisation was conducted at 70°C for about 4 hours, to ensure complete monomer conversion. The reaction mixture was then filtered whilst hot and dried.

The resultant product was examined by transmission electron microscopy to observe the degree of encapsulation. The conversion of monomer to polymer was determined by thermal analysis, and zeta potential measurements were made of base pigment, encapsulated pigment and a normal inorganically coated pigment.

Various modifications were made to the initial system and variations in procedures and techniques have been investigated. However, this proprietary information will not be discussed here.

Uses of ultrasound-sonochemistry

The first commercial application of ultrasound was in 1917 when Langevin applied it to the detection of icebergs. However, the use of ultrasound in promoting chemical reactions is a much younger science and the discipline of sonochemistry is awaiting exploitation.

In our work, we have collaborated with one of the premier schools of sonochemistry led by Dr. T Mason and Dr. J. P. Lorimer, Coventry Polytechnic.

Ultrasound is a name given to sound waves having

frequencies higher than those to which the human ear can respond (i.e. > 16kHz). The upper limit of ultrasonic frequency is not sharply defined but it is usually taken to be 5 MHz for gases and 500MHz for solids and liquids.

Being a sound wave, ultrasound is transmitted through any substance, solid, liquid or gas, which possesses elastic properties. The movement of the vibrating body (i.e. the sound source) is communicated to the molecules of the medium, each of which transmits its motion to the adjoining particle, before returning to approximately the original position again. It is this movement of molecules, producing areas where there is a deficiency of molecules, which gives rise to the alternate compression and rarefaction portions of the wave.

The chemical effects of ultrasound arise from the physical processes that create, enlarge and implode gaseous cavities in a liquid. During the expansion cycle, a sound wave of sufficient intensity can generate these cavities. A liquid is held together by attractive forces and in order for a cavity to form, a large negative pressure associated with the expansion cycle of the sound wave is needed to overcome the attractive forces. The cavity will grow and reach a critical size where it will most efficiently absorb energy from the ultrasound. It then reaches a point where it can no longer absorb energy, liquid rushes in and the cavity collapses.

The implosion of cavities generates intense heat that raises the temperature of the liquid around the cavities and causes an immense pressure rise.

The sonochemistry of liquids depends mainly on the physical effects of the heating and cooling caused by cavity implosion. It is only since 1945 that a rapid expansion in the application of ultrasound to chemical processes has occurred. Ultrasound has become an important tool in studying a range of topics such as analysis and relaxation phenomena, organic synthesis and polymerisations[12,13].

In our encapsulation process, for at least part of the time, the polymerisation components are subjected to ultrasonic vibrations, where power output in the range 65 to 125 watts per litre of material is used. This was achieved with an ultrasonic probe immersed in the reaction vessel (Figure 1.1) and was used according to three different schedules, i.e.

Figure 1.1
Ultrasonic probe
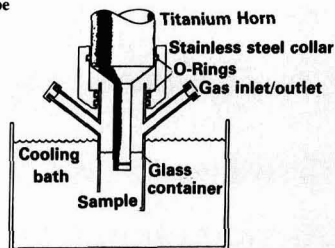
1. During initial stages of polymerisation, up to, and including, addition of monomer.
2. During the latter stages of polymerisation, after addition of monomer.
3. During the whole polymerisation.

Future developments

Figure 2 shows transmission electron micrographs of TiO$_2$ coated with polymethyl methacrylate (a) using ultrasound and (b) without ultrasound. Ultrasound is believed to enhance polymerisation reactions by the sequence of

processes described earlier. There are obvious differences between the product of our encapsulation process using ulstrasound than following a conventional method.

Figure 2
Transmission electron micrographs of encapsulated TiO$_2$ pigment (a) using ultrasound and (b) with no ultrasound
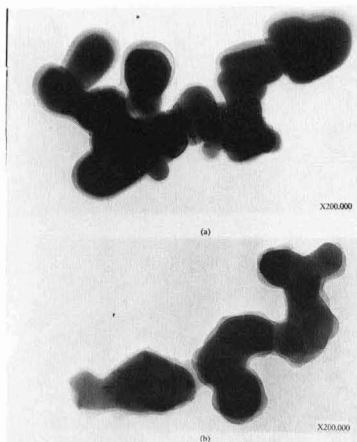
Encapsulation with ultrasound

It is apparent from our results that the use of ultrasound leads to a polymer coating, considerably thicker and more consistent than without ultrasound. The reason for this is that ultrasound is promoting polymerisation to occur more at the pigment surface than in the bulk. It has been suggested[14] that sonication will clean the surface of the TiO$_2$, hence enhancing its chemical reactivity. This may be what has been observed in these experiments.

Experiments were carried out, as described in the experimental section, at different power outputs. It was discovered that the state of encapsulation depended on the particular power chosen and at which point in the process the ultrasound was applied to the reaction mixture. Figure 3 shows transmission electron micrographs of encapsulated material having been subjected to ultrasonic vibrations at (a) 22 watt output in initial stages, (b) 55 watt output in initial stages, (c) 47 watt output in latter stages of polymerisation and (d) 28 watt throughout the entire reaction.

It was observed that the most beneficial effect was obtained when ultrasound was applied only in the initial stages of the reaction. Also the use of lower powers improved the coverage compared with higher powers, but higher powers produced better dispersion of the coated particles.

Experiments carried out at acid pH appeared to give a greater degree of encapsulation than those carried out at alkaline pH. pH monitoring throughout the reaction indicates that the dispersion is more acidic once the polymerisation is complete.

Encapsulation without ultrasound

Figure 2 (b) indicates that without the application of ultrasound to the reaction mixture polymer coatings can still be produced. However, they are less uniform and are not as thick as those produced with ultrasound.

Figure 3

Transmission electron micrographs of encapsulated TiO₂ pigment having been subjected to ultrasonic vibrations at (a) 22 watts in initial stages (b) 55 watts in initial stages (c) 47 watts in latter stages and (d) 28 watts throughout the entire reaction.

Effect of ultrasound power on encapsulation:

(a)   (b)

(c)   (d)
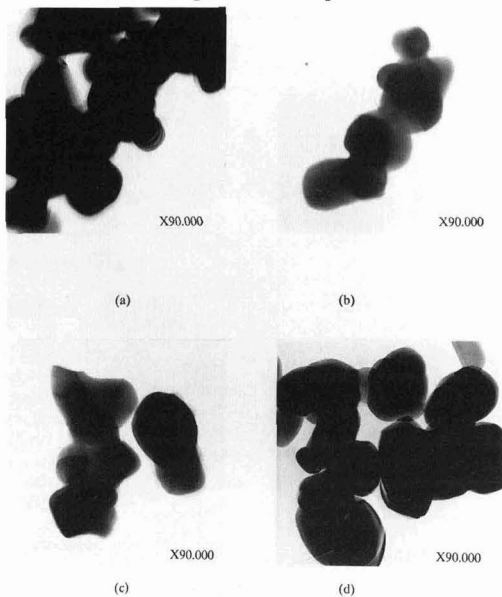
Pre-treatment of the pigment

Table 1 shows the results of polymerisations after pretreatment with various surfactants, and the dispersibilities of the dried product in water and hexane.

Table 1

Surfactant (cmc/25°C) mol/dm³	Concentration (c/10 mol/dm³)	% Conversion	Dispersibilities	
			Water	Hexane
(a) Triton-X-100 (2.04 × 10⁻⁴)	0.50 × 10⁻⁴	94.80	No	Yes
(b) Triton-X-100	0.50 × 10⁻⁴	80.20	No	Yes
SLS (8.1 × 10⁻³)	6.25 × 10⁻³	80.90	No	Yes
SLS	8.00 × 10⁻³	60.70	No	Yes
SDS (8.27 × 10⁻³)	11.70 × 10⁻³	40.20	Slight	No

Triton-X-100 = iso octylphenoxypolyethoxy ethanol
(a) Triton-X-100 = with ultrasound
(b) Triton X-100 = without ultrasound
SLS = Sodium lauryl sulphate
SDS = Sodium dodecyl sulphate

The dispersibilities correspond to the degree of encapsulation, the more uniform the coverage of polymer the better the dispersibility in hexane and the worse in water. Triton-X-100 with ultrasound gave the best polymer coverage and the highest conversion. The best results were also obtained by working below the critical micelle concentration (cmc) of each surfactant.

Addition of some surfactant prior to the monomer resulted in a more uniform polymer coating (Figure 4). Pre-treating the pigment with surfactant molecules allows them to form an adsorbed layer on the surface. Monomer molecules and radicals in water are absorbed into the layer in which polymersation will preferentially proceed and a polymer coating is formed. It was observed that an ionic surfactant gave better results than a non-ionic surfactant as the pre-treatment agent, since ionics have higher cmc's.

Figure 4

Transmission electron micrograph of encapsulated TiO₂ after pre-treatment with surfactant.
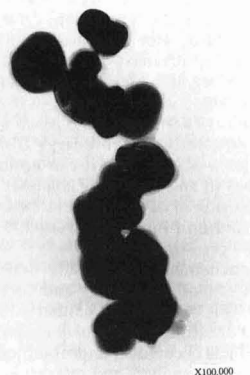
Reaction conditions

Considering the addition of monomer to the polymerisation mixture, it was found that a seed and feed method gave the greatest, most uniform polymer coverage (Figure 5). Other methods tried included one addition of monomer in the initial stage and another in the latter stages of the polymerisation.

In Table 2 the effect of initiator concentration on the polymer content is illustrated. It was observed that a single addition of redox initiators presented a uniform polymer coating, at high coverage. Transmission electron micrographs in Figure 6 support the results represented in Table 2.

Figure 5

**Transmission electron micrograph of polymer encapsulated TiO₂, obtained by a seed and feed addition of monomer**

Table 2

Polymerisation at different initiator concentrations

Pigment	Initiators		Polymer Content
	(g/l)		(%)
TiO₂	$K_2S_2O_3$	$Na_2S_2O_5$	
R-TC90	0.067	0.047	26.00
	Single addition		
R-TC90	0.027	0.014	11.37
	0.080	0.056	
	Dual addition		
R-TC90	0.013	9.4×10^{-3}	6.47
	0.040	0.029	
	Dual addition		

Figure 6

Transmission electron micrographs of polymer encapsulated TiO₂ with (a) a single addition of redox initiators (b) dual addition of initiators at increased concentration and (c) dual addition of initiators at a reduced concentration

Effect on initiator concentration on encapsulation:
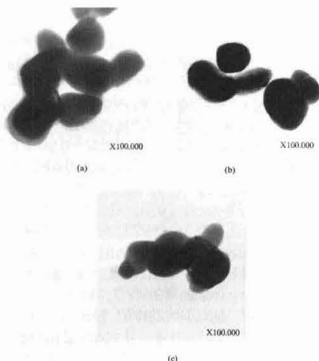
Polymerisation with the redox initiators appeared to proceed more rapidly and produce a more uniform polymer coating than using potassium persulphate alone as the initiator. Other initiators evaluated included azo compounds (e.g. AIBN), benzoyl peroxide, butyl hydroperoxide with sodium metabisulphite and hydrogen peroxide. All of these were less successful than the redox couple, $K_2S_2O_8/Na_2S_2O_5$.

Zeta potential measurements were obtained of the base pigment, the polymethyl methacrylate coated pigment and polymethyl methacrylate latex particles (Figure 7). There is a definite similarity of shape in all curves and the pH values at the isoelectric point are approximately 5 for all three. The encapsulated pigment has a much higher negative zeta potential than the base pigment, hence a higher negative surface charge. This implies that it is most likely to be more stable in an emulsion paint system which tends to be alkaline

in nature having a pH at around 8-9.

For some pigments e.g. barium sulphate it was found that the surface charge can easily be reversed by lowering the pH below 7. However, if the pH is too low it may be unsuitable for polymerisation.

Figure 7

Zeta potential measurements

(a) Base TiO2 pigment

(b) Encapsulated TiO2

(c) Latex particles of polymethyl methacrylate
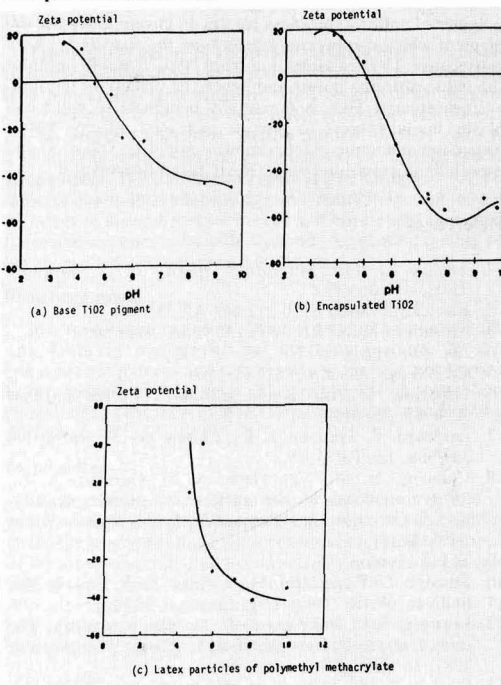
In our process, aluminium nitrate was added initially to the dispersion to attain a high cationic charge density. However it seemed only to work efficiently if it was added in combination with a weak acid, usually an organic acid e.g. methacrylic acid. The aluminium nitrate at the pH of our experiments exists as Al^{3+} and it could be assumed that at this pH the Al^{3+} exchanges with a proton of the methacrylic acid, hence the need for both in our polymerisations. There are obviously alternative explanations as to the role of Al^{3+}, in fact it could also be possible for it to lay itself down on the pigment surface, prior to the coupling with the acid. The amounts of aluminium nitrate and organic acid were found to affect the polymerisation. The amount need only be sufficient to achieve the desired charge effect on the surface, to activate it. Our experiments show that a ratio of Al^{3+}: acid of 3:1 produced the best, most consistent results. Salts, other than aluminium nitrate have been tried i.e. aluminium sulphate, calcium nitrate, zinc nitrate, titanium tetrachloride and zirconium nitrate.

Future developments

Evaluation of polymethylmethacrylate coated pigments is now required in many practical applications, including emulsions and plastics, to assess their potential. Also, in order to allow flexibility in producing specific pigments for specific applications it is planned to use other monomers in the encapsulation progress eg. styrene and butyl acrylate.

Conclusion

In this paper, a new method of encapsulating TiO$_2$ pigment with a uniform polymer coating has been described.

The procedure involves the emulsion polymerisation of methyl methacrylate using ultrasonic vibrations during part of the reaction.

As suggested in this paper, encapsulating TiO$_2$ with a polymer of uniform thickness creates an envelope around the pigment which can precisely determine the spacing between consecutive TiO$_2$ particles in a paint film. This will optimise the light scattering power and hence the opacity of the film.

Encapsulated TiO$_2$ is potentially beneficial to paint and plastic manufacturers to provide increased opacity, better dispersion and improved mechanical properties (plastics) and especially in emulsion paints, for reduced flocculation.

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Based on paper presented at the 1990 PRA Symposium on Emulsion Polymerisation.

Summary

From our experiments it is concluded, that the temperature T_{min} which is a temperature when the film thickness has its minimum related to bath temperature for a given system is proportional to viscosity of the deposited uncured film in the electrodeposition process. Furthermore the uncured film viscosity is related to the resin chemistry and/or paint formulation.

Electrochemical datas and photomicrographs by SEM of freshly coagulated films indicate different deposition processes depending on bath temperature.

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Exterior decorative coatings for wood — A US overview

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Introduction

Products for the protection and decoration of exterior surfaces in the US vary significantly from those in the UK. The differences are in both the formulation types and the relative proportions of products sold. This can be ascribed to the unique combination of factors — building materials, consumer needs and perceptions, and marketing strategies — prevalent in that country. While this presentation is a brief, descriptive overview of these topics as they relate to coatings for exterior wood, other materials and paint products will be mentioned as well, especially when their use impinges upon the traditional use of wood.

Substrates and construction

Wood frame construction is by far the most common type used in the US housing market. Most recently, major changes have been made in the use of prefabricated structural components, sheathing materials, and insulation in order to reduce construction times and costs and energy consumption for the owner. This 'tighter' construction has had a major impact on paint failures and, in some instances, failures of the structural members and cladding materials, due to moisture entrapment in wall cavities. Blistering and peeling is the most common form of paint failure in any part of the country with a significant heating season. The ability of latex paints to transport moisture vapour more readily thus becomes an important factor in coating selection.

Wood is only one of a number of cladding and exposed structural materials used in the construction of the homes and small commercial properties commonly painted with decorative products. While speciality coatings exist for some of these materials (e.g. repainting coil coated aluminium siding) exterior decorative products are generally expected to perform on all of them.

Wood

Over the years wood has been the major cladding, trim, and joinery material in US housing construction, however its use has been significantly reduced in the last two decades due to availability and cost. Wood cladding (siding in US terminology) is mostly western red cedar and redwood although various species of pine are also used and older homes may be clad with any of a number of regionally available hard or soft woods. Trim pieces and window and door joineries are usually made of pine. Wood cladding is predominantly in the form of lap siding although smooth or striated shingles and drop siding are also common.

Plywood

Plywood sheets are commonly used in exterior construction for eaves, insets over and under windows and doors, and for garage doors. More recently, specially faced plywoods have found significant use as a primary cladding material, imitating 'board and batten" or tongue and groove construction with either rough sawn or smooth textures. Coating plywood involves unique challenges as the method of manufacture insures stress cracking of the upper layers of the laminate with resultant stresses being applied to the coating. This has been made worse by the continual reduction in the quality of materials used in the production of all types of plywood.

Hardboard

Hardboard is a class of composite cladding materials made from wood fibres mixed with resin and formed into sheets at high temperature and pressure. They often contain wax or other materials to increase their water resistance. Hardboard can be supplied unprimed, factory primed, or fully coated. The surface can be smooth or embossed to simulate wood grain effects. The painting or repainting of hardboard can be difficult due to its tendencies to swell, exude wax, and to lose its integrity around surface breaks and bare edges (e.g. nail holes and cut ends). As with plywood, the general quality of hardboard has decreased in this decade.

Structural wood

Structural wood materials, usually pressure treated planks and framing members, are used extensively in the construction of decks and porches where they are not framed in or hidden by cladding. The nature of the pressure treatment and the total time left unpainted can make painting difficult.

Metal siding

Metal cladding is mostly coil coated aluminium referred to as aluminium siding. These products were the first major challenge to wood siding in new construction and were as well as the major material used to cosmetically improve old homes with serious paint failures over wood. New siding can be difficult to paint due to the coil coating's hardness and use of mar resistance additives, while weathered siding, especially white, can be heavily chalked down to almost bare metal.

Vinyl siding

Aluminium's biggest competitor, vinyl siding is a solid moulded plastic, coloured throughout, often combined with a backing of foamed insulation. Its advantages over aluminium siding are cost, weight, resistance to denting, and less noise in windy conditions. As with early aluminium sidings, vinyl manufacturers make a 'never need painting' claim. Early vinyl siding and guttering did embrittle in a relatively short time and, as the failure was throughout the material, replacement rather than painting was required. Currently, the painting of vinyl siding for decorative or protective purposes is in a rather nebulous state in the US.

Masonry

Rendering comprises a relatively small percentage of exterior surfaces in the US, although it is popular in some regions, most notably the south and southwest where Spanish influences are greatest. Block, brick and cement/fibre board are also used for both houses and commercial properties. These materials are usually painted with masonry products very similar to those available in the UK.

The consumer

The postwar US decorative paint market has been driven by the retail market. In the interior area this was reflected in the very early conversion to waterborne coatings and roller application, both increasing ease and speed. Similarly, in the exterior area the move to waterborne convenience began early; successful latex exterior paints were in place by the

mid-60s. These products were resisted by the tradesman and the 'knowledgeable' DIY painter and it wasn't until the 1970s that the extended durability and improved moisture vapour transport of acrylics were generally recognised.

While exterior latex paints were initially accepted by the consumer for convenience reasons, the long term impact of that acceptance on consumer perceptions of paints should not be underestimated. Although the original latex exterior paints were tolerated even though they were matt finishes with poor flow because their ease of application (especially on the large surface areas prevalent in the US) and clean up, they gradually became accepted as a standard decorating style — even on some trim. In other words, there was a lowering of the general expectations of appearance. When latices were developed to give moderately high gloss in exterior formulations most of the remaining trim and cladding painting converted from solventborne quite quickly. The significantly lower gloss and poorer flow characteristics were outweighed by convenience and the fact that flat, ribby paints were already accepted in the market and the new products were better than those. This lower standard of gloss has become the norm in the US and there is presently very little market for truly high gloss materials — either interior or exterior.

It should be noted that the consumer acceptance of latex products for convenience has not been all-encompassing. The acceptance of latex stains has been much slower than the products cited above. Consumers have an intuitive perception of the difficulties associated with making a stain with a non-penetrating, film forming, waterborne latex. The tendency of these products to fail, like paint, by cracking and flaking justifies their distrust.

Products

House paints

The largest category of exterior paint products in the US is paint for exterior cladding, generally referred to as house paint. These products — especially gloss house paints — are also used for most trim and joinery. Latex mattes (flats in the US) are the biggest seller in this group. A quality flat house paint is usually based on an acrylic resin and has a volume solids of 33-40%, 20% TiO_2 by weight, and a PVC under 40%. Traditionally, major manufacturers have modified their flats with a long oil alkyd or bodied oil for adhesion to chalk and dirt and zinc oxide for mildew resistance. Improvement in latex adhesion technology has reduced the use of alkyd/oil modification while cost and stability problems have almost eliminated the use of zinc oxide.

Latex gloss house paints are also usually acrylic-based with lower total PVC than mattes (ca. 20% for whites). The need to develop and maintain reasonable gloss means that these products have never been formulated with either alkyd or zinc oxide modification. Consequently, many of the early products had marginal adhesion and mildew resistance properties. Much of the resin suppliers' research in the 1970s and 1980s has gone into improving the adhesion to dirt and chalk of their latices for gloss house paints.

The smallest segment of the house paint market is now solventborne products. These are quite similar to the exterior gloss paints available in the UK. They are based on medium to long oil alkyds produced from soya, linseed or tall oil fatty acids. One difference is that the US generally does not expect or desire the high 20° specular component found in UK gloss products.

Most US exterior paint systems are two component only — undercoat (primer in US terminology) and topcoat. The undercoat is almost always recommended for bare wood (new or redecoration) but is not used on repainting sound surfaces. Both undercoat and topcoat are used one coat except in circumstances where the protection of a marginal substrate (e.g. hardboard) is paramount and an extra undercoat or topcoat is recommended. Although latex undercoats are available from most manufacturers and give better crack resistance properties on most woods, the frequent use of staining woods such as cedar and redwood necessitates the use of alkyd undercoats to avoid tannin staining. Hardboard is another instance where the use of alkyd undercoats is often recommended in order to reduce the chance of face and edge swelling.

Having described 'typical' US house paints, it should be noted that cost pressures since the 1970s oil crisis and changes in marketing strategies have complicated the rather simple situation described above. By the middle-to-late 1970s many manufacturers had developed latex flat house paints based on significantly lower volume solids and higher PVC. Costing less than their traditional counterparts, the best of these formulations also had improved hiding characteristics as well as lower dirt pickup due to reduced surface thermoplasticity. The obvious disadvantages were lower extensibility and poorer overall protection of the substrate (thinner, more porous films). Some of these formulations were sold as first quality products, others as lower priced entries into the market. Marketing strategies, following the example of high volume, highly segmented consumer products (e.g. beverages), have also emphasised breadth of product offering and niche marketing. Thus it is not unusual for a major manufacturer to offer house paints at three gloss levels with two or more price points for each.

A good example of the development of market segments through the synthesis of marketing and consumer expectations is the development of a new house paint category in the 1980s — exterior eggshell or mid-sheen products. With the increased use of exterior coil coated aluminium siding which is usually supplied with a low 60° gloss and a moderate to high 85° sheen, consumers gradually began to accept and appreciate this 'soft gloss' effect. As more aluminium siding needed to be repainted a demand for a product with a similar specular profile could be stimulated or fulfilled — depending on your view of the marketing process. Now most major US manufacturers offer at least one such product and they are being used on all types of cladding.

Stains

Exterior stains in the US are unlike the resin-rich, somewhat glossy products sold in the UK, although cladding stains much more like US products are now being offered. US products are designed to cover large surface areas and are generally formulated without structure and at low viscosity making them among the most difficult exterior products to apply. They are formulated in both semi-transparent and opaque qualities, with the latter designed to show only the texture of the wood, not the variations in grain colour. Much of the volume of stains is now applied to various forms of plywood claddings.

As noted earlier, latex products have made fewer inroads into the stain market than in other exterior areas due to their tendency to act as thin surface films. Most latex stains are acrylic-based 'paints' at low volume solids and PVC and do give excellent colour retention. The more popular solventborne products are generally alkyd-based, although one major manufacturer still uses an oil-based formulation claiming that it still gives the best penetrating and 'restorative' properties.

The resurgence of the use of natural wood design elements in housing and small commercial buildings, along with the growing popularity of decks and porches made of pressure treated wood, has resulted in a boom market for stains and related products. In recent years estimates have been made that decks and porches are being added to existing housing by

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Transport through polymer latex films in relation to morphology

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Abstract

Thin films produced from poly (butyl methacrylate) latices made by surfactant-free emulsion polymerisation have been studied with regard to their permeabilities to gases, vapours and aqueous solutes and their morphologies examined by a freeze-fracture replication TEM technique. Film preparation time and temperature and ageing time and temperature influenced the state of coalescence of the films and their permeabilities. Common additives and impurities post added to the model colloid latex were investigated and did not necessarily produce the deleterious effects on film quality which might be anticipated.

Introduction

Environmental pressures have led to greatly increased interest in applications of aqueous-based latex coatings. A continuing problem with latex coatings is their higher permeability, compared with solvent-based films, towards water vapour and air pollutant gases.

Most experimental studies of film transmission properties have been of films produced by solvent casting, compression moulding, extrusion etc., with latex films receiving comparatively little attention. When a latex is dried by evaporation of water from its surface the polymer particles are driven together until the stabilising forces (electrostatic or steric) are overcome and for a soft latex i.e. one above its minimum film formation temperature (MFFT) a continuous film forms by coalescence of the polymer particles. Theoretical treatments[1-5] of the process have invoked capillary forces, interfacial tensions and sintering overcoming the shear modulus at the MFFT. The deformed particles are held together by physical forces then undergo further gradual coalescence and film mechanical properties improve[6]. That coalesced clear films are necessarily completely homogeneous has been disputed by Distler and Kanig[7] who observed, using a staining technique and transmission electron microscopy, a honeycomb pattern of interparticle boundaries.

The aim of the work described here was to use surfactant-free latices (model colloids) to prepare latex films and study their transmission properties in relation to the film morphology.

Experimental

Surfactant-free latices of uniform particle size were prepared and cleaned as described previously[8]. Film preparation in the absence of surfactant poses extra problems since substrate wetting is inferior on hydrophobic surfaces with disjoining tending to occur but for hydrophilic substrates, although wetting is not a problem, then film detachment is difficult. These problems were overcome in different ways in three separate aspects of this work.

(a) *Films spray cast and their helium permeability studied[9].*

The aim was to form the polymer film so quickly on a PTFE surface that it did not disjoin. This was achieved by spraying the latex on to a heated block, coated in PTFE, at temperatures in excess of 120°C. Multiple passes (20-50) of the spray gun were employed and the film was then allowed to return to room temperature before removal and in some cases cooled further, using a CO_2 slush bath, closer to the Tg of the polymer. The permeability coefficients to helium were measured using a dynamic technique in which the penetrant flowed over one side of the film and the permeating gas was swept from the other side by nitrogen and its concentration determined using a Katharometer. The principal feature of PBMA latex film permeability, (the polymer most used due to the film handling characteristics) was that P depended on the coating temperature in the range 120-182°C and then dropped over a period of 320 hours to a near constant value which was still more than double the value for solvent cast film of the same polymer (whose permeability did not change over several months). Polymers of lower Tg aged faster whilst poly(ethylacrylate) appeared to age fully during coating. No effects of particle size or surface charge density were discerned presumably as a result of the high temperature necessary for the flash casting process.

(b) *Films cast on Pyrex glass plates, removed by soaking in warm water and nitrophenol solute permeability studied[10].*

A glass cell consisting of two identically stirred compartments was used to centrally mount the latex film with nitrophenol solution in the donor compartment and pure water in the receiver compartment. The nitrophenol content in the receiver side was measured continuously using a flow cell in a UV spectrophotometer. PBMA latex films were prepared over a range of temperatures 52-95°C and times 3-20 hours (Table 1). The higher the temperature and the longer the time, the lower was the initial permeability. Each of these films aged to a lower permeability upon storage (Table 2). Ageing rates were enhanced at elevated temperatures and slowed at sub ambient temperatures. Activation energies increased reflecting decreased permeability and reached 142 kJ mole^{-1} for a film prepared at 95°C and aged one month at ambient (Table 3). A freeze fracture replication TEM technique was used to show interparticle boundaries in latex films. A uniform close packed dodecahedral structure could be identified and the clarity of the interparticle boundaries depended on the time and temperature of preparation (Figure 1). Only at 120°C was there no remaining evidence of particle structure when the fracture cross section resembled that of a solvent cast film (Figure 2).

Replicas of the two surfaces of a latex film revealed slippage of layers of latex particles at the upper surface presumably arising from stress during drying (Figure 3). The substrate side was smooth (Figure 4) and the film asymmetry was also manifest in the permeability. When the face towards the nitrophenol donor solution was the lower (substrate) side then the greater permeability was observed. This was interpreted in terms of nitrophenol desorption from the film being the rate determining process. An opposite trend was observed for solvent cast films, since in that case it was the upper surface which had a skin of greater density (Table 4).

Figure 1

PBMA Latex film cast at room temperature
A=hexagonal cross section of a particle,
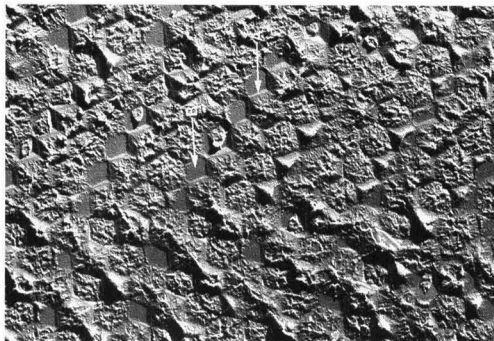B=smooth diamond face of a particle in layer below

Figure 2

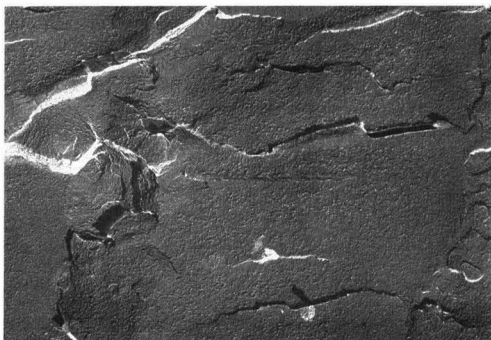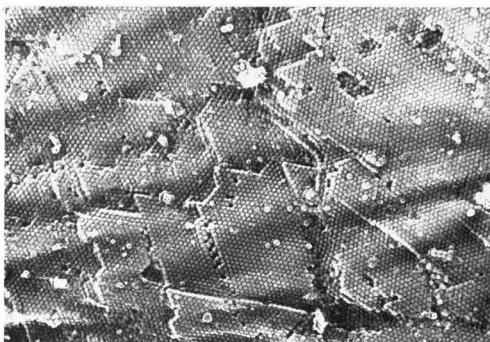PBMA Latex film aged at 120°C for 60 Hours

Figure 3

Replica of air surface of PBMA latex film

Mercury porosimetry and BET krypton adsorption measurements were applied to both latex and solvent cast films. An apparent uptake of mercury at high pressures was attributed to film compressibility since in contrast a film with designed porosity was readily analysed by porosimetry. The BET surface areas for both solvent and latex films were greatly in excess of the geometric areas of the films used and the values were similar for both types of film (Table 5). It is

tentatively suggested that microporosity may have been introduced into the films at the low temperature (77K) of the experiment. It could not resonably be attributed to the free volume in PBMA so far below its Tg.

Table 1

The effect of casting time and temperature

Permeability coefficient/10^{-10} m^2 h^{-1} after 24 hours at room temperature

Drying temperature	Drying time/hours		
	3	6	20
52	—	—	12.2
66	—	—	5.4
80	9.9	6.2	2.3
95	4.5	2.5	*

Table 2

The reduction in permeability coefficient with time for films aged at room temperature

Film age/ Hours	Permeability coefficient/ 10^{-10} m^2 h^{-1}
24	9.9
48	4.2
72	4.4
96	3.1
144	3.3
336	3.9
504	3.6
672	2.8

Table 3

Activation energies for latex films prepared under a variety of conditions

Permeability coefficient/ 10^{-10} m^2 h^{-1} at 30°C	Activation energy/ kJ mol^1
4.8	69.9
4.6	73.9
4.5	67.3
4.2	68.7
3.6	84.6
2.9	84.4
2.8	88.1
2.5	89.9
2.1	103.3
1.2	96.2
0.12	142.0

Table 4

Nitrophenol permeabilities and film asymmetry

Latex Film Side facing Donor	P/10^{-10}m^2 h^{-1}
Upper (air)	4.3
Lower (substrate)	9.2

Solvent Cast Film Side facing Donor	P/10^{-10}m^2 h^{-1}
Upper (air)	9.8
Lower (substrate)	7.7

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Figure 4
Replica of substrate surface of PBMA latex film
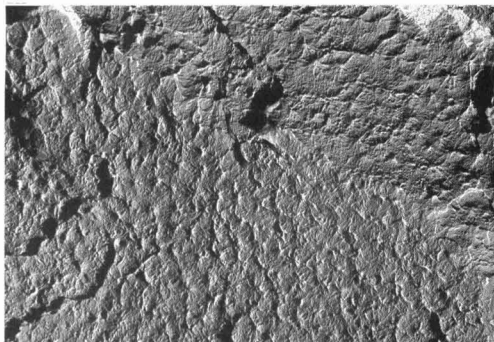
(c) *Additive present films cast on Nylon plates and their water vapour permeabilities studied[10].*

Additive present films were cast on nylon plates from which they would be removed without the need for soaking. Additives included surfactants of common C_{12} hydrocarbon chain length but differing head group functionalities i.e. sodium dodecyl sulphate, (S.D.S.) dodecyl dimethyl, ethyl ammonium bromide (D.E.D.A.B.) and dodecyl hexaoxyethylene glycol monoether, ($C_{12}E_6$). Water vapour permeabilities were determined by a method similar to that used by Banker[11]. 10 cm^3 glass sample bottles were used containing 5 cm^3 of saturated ammonium sulphate and the film was fixed to the top of the bottle using a concentrated solution of PBMA in butanone as adhesive. The test bottles were stored in a desicator and removed periodically and weighed over an eight day period. A minimum in film permeability was found at monolayer coverage of SDS (Table 6) and this was interpreted as being either a consequence of improved particle packing order due to enhanced charge stability or to surface plasticisation by SDS since somewhat greater coalescence was apparent in freeze fracture TEM replicas. Below monolayer coverage permeability decreased with increased concentration and tended to age to lower values. At high SDS concentrations P increased and islands of SDS could be seen on micrographs as small aggregate defects and also smaller aggregates in the interparticle interstices. Particle boundaries could be observed and the films did not age to lower permeabilities (Figure 5). For the cationic surfactant, at concentrations sufficient to give charge reversal and maintain stability, a minimum was observed at

Figure 5
PBMA latex film with excess S.D.S. added
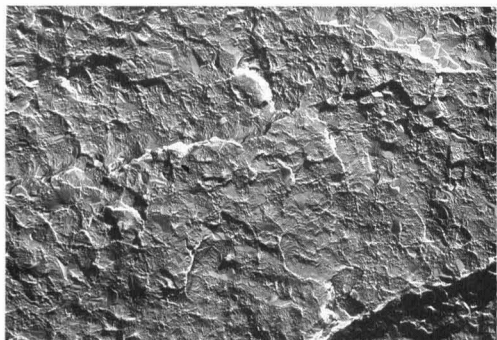
Figure 6
PBMA latex film with added KC1
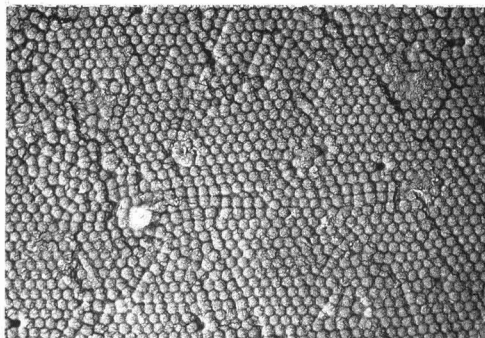
monolayer coverage but permeabilities were higher than for SDS addition and for clean films (Table 7). Speculatively, interfacial salt formation by surfactant and latex surface groups causing increased hydrophilicity could be invoked to explain this effect. Significantly different behaviour was observed for $C_{12}E_6$ which plasticised films making them more flexible but not tacky. Increased coalescence with slightly reduced permeability at surface coverage was observed but then permeability increased with concentration. Being well coalesced the films did not age to lower permeabilities (Table 8)..

For post added inorganic electrolyte (KC1) below the critical coagulation concentration of the PBMA latex (Figure 6) a reduced packing order and enhanced permeability was observed with most of the salt being exuded from the interstices to the surface layers, a tendency which increased on ageing.

Conclusions

The freeze fracture replication/TEM technique employed is useful in identifying interparticle structures in latex films. The removal of surfactants from latices thereby reducing the hydrophilic content of the film does not necessarily reduce the water vapour premeability of the film since a minimum in permeability can be observed at monolayer coverage of surfactant. The initial permeabilities of latex films depend upon the temperature and time of film formation and conditioning but deliberate exploitation of these differences, in e.g. controlled release applications, is negated by significant reductions of permeability upon aging towards a common value.

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Table 5

Mercury penetration and Krypton adsorption

Film	Culmulative Pore Volume Hg/mm^{3}g^{-1}	B.E.T. Surface Area Kr/m^{2}g^{-1}
PBMA latex (80°C)	37	0.37
PBMA latex (>120°C)	45	0.24
PBMA solvent cast	33	0.31

Table 6

The effect of added SDS on water vapour permeability

Conc SDS/ mole/gram polymer 10^{-6}	water vapour permeability coefficient/ 10^{-17} s m^{3}kg^{-1}			
	Initial film orientation to vapour		After 1 month film orientation to vapour	
	Lower	upper	lower	upper
0	2.1±0.29	3.1±0.56	1.4±0.10	
78	1.8±0.06	2.8±0.33	1.2±0.01	2.0±0.1
150	1.0±0.09	1.0±0.08	0.9±0.07	0.9±0.07
178	1.8±0.07	2.2±0.22	2.2±0.08	2.3±0.04
258	2.5±0.16	3.4±1.85	3.5±0.28	5.6±0.78
350	2.7±0.08	2.7±0.26	2.8±0.48	3.3±0.40

Table 7

The effect of added DEDAB on water vapour permeability

Conc DEDAB/ mole/gram polymer 10^{-6}	water vapour permeability coefficient/ 10^{-17} s m^{3}kg^{-1}			
	Initial		1 month	
	lower	upper	lower	upper
0	2.1±0.45	3.1±0.56	1.4±0.10	
138	4.6±0.31	6.2±0.62	5.1±0.29	6.0±0.35
164	3.4±0.42	5.2±0.09	4.3±0.11	5.7±0.03
258	4.8±0.008	4.2±0.30	4.4±0.36	4.5±0.08
350	4.1±0.28	4.1±0.28	4.5±0.14	5.3±0.07

Table 8

The effect of added C12E4 on water vapour permeability

Conc C12E4/ mole/gram polymer 10^{-6}	water vapour permeability coefficient/ 10^{-17} s m^{3}kg^{-1}			
	Initial film orientation		1 month film orientation	
	lower	upper	lower	upper
0	2.1±0.45	3.1±0.56	1.4±0.10	
75	1.9±0.16	2.2±0.29	2.3±0.3	3.5±0.66
150	3.0±0.18	3.1±0.22	3.3±0.23	3.5±0.11
250	3.3±0.27	3.7±0.12	3.6±0.05	4.2±0.11
325	3.1±0.27	3.2±0.05	3.5±0.50	3.2±0.17

Based on paper presented at the 1990 PRA Symposium on Emulsion Polymerisation.

the hundreds of thousands per year. Although most have been built using pressure treated timber and left initially uncoated, aesthetic and surface weathering considerations mean that most will receive some form of decorative or protective surface coating shortly into their projected life span. Traditional stains are now vying with a multitude of speciality products — weathering stains, water repellent stains, clear treatments, preservative stains, and wood 'restorers' — for the consumer's attention. It is also interesting to note that the small-to-medium decorators have also been able to exploit the increased profile of stain products. Many now offer to blast or chemically strip houses with a history of paint peeling problems down to bare wood and then apply solventborne stains, thus 'eliminating' the home owner's paint problems.

Legislation and development trends

An area which has a significant impact on the entire US paint market is environmental legislation — specifically limitations on the volatile organic content (VCO) of surface coatings. Excepting some speciality products such as varnishes, the current limit for decorative products is 250 to 380 grams VOC per litre of dehydrated paint (i.e. the total paint formulation minus water). While most latex paints comply, difficulties can arise when formulating latex gloss products with high glycol levels for open time or large amounts of high glycol content universal tinters. Some of these products will need significant formulation changes if levels are reduced further. In solventborne systems the biggest problems are in low solids formulations such as stains. Here the use of higher solids with lower molecular weight resins can give formulations within the legislated target, but at a large price penalty.

Beyond legislative pressure, development trends in the US paint industry will continue to be driven by the combined influences of cost, marketing strategies and technological advances. Market segmentation and niche product exploitation will continue, while improvements in adhesion promotion, rheological control and non-pigmentary opacifying materials will move more quickly into the exterior formulating arena as price/performance pressures become even greater. ■

JANUARY JOCCA

GREENER COATINGS

Ontario Section

Aqueous acrylic polymers and pigment dispersion

At the last technical meeting of the 1989-1990 session on May 16, 1990, the speaker was Mr Gary Wulf of S. C. Johnson and Son Inc., Racine, Wisconsin.

Mr Wulf began by stating that, although a polymer normally will be in the solution form when it is used as a dispersion vehicle, the physical form in which the polymer can be manufactured is dictated by the molecular weight (Mw):

- Soluble solid grade or flake resins can be produced in the range of roughly Mw 2,000 to 12,000;
- Neutralizable emulsions cover the range of about Mw 25,000 to 100,000 or higher;
- Products in the intermediate range can be made by direct solution polymerization.

He explained that the most significant properties of aqueous acrylic vehicles are molecular weight, acid number and hardness (as indicated by glass transition temperature, Tg), and showed that the selection of a suitable dispersion vehicle follows from these considerations:

- Higher molecular weight produces higher viscosity (or lower solids at the same viscosity);
- Higher acid number (indicating a higher degree of carboxylation) increases the ability of the polymer to be dissolved by water and to wet polar surfaces;
- Higher Tg indicates higher heat resistance, less flexibility and poorer adhesion.

Considering the selection of dispersion vehicles according to the types of pigment being dispersed, these generalizations were made:

- Organic pigments work best in vehicles having relatively high acid number and low molecular weight (low viscosity), as do high quality surface treated carbon blacks;
- Low cost (untreated) carbon blacks are more easily dispersed in low acid number polymers;
- Inorganic pigments such as china clay, iron oxides and surface-treated TiO_2 usually present no problem and can be dispersed in polymers having a wide range of properties.

Mr Wulf then discussed how specific properties of finished inks can be enhanced by the selection of acrylic vehicles according to their polymer properties:

- Alkali resistant and water resistant inks require vehicles having low acid number (for minimum resolubility);
- Heat resistant inks call for vehicles having high Tg (as well as high softening point);
- High gloss requires polymers of low molecular weight and high acid number, in order to get the maximum vehicle solids into the system;
- Adhesion and flexibility are greatest with both solutions and emulsions having low Tg, and with a high emulsion-to-solution ratio;
- Drying is faster with emulsions than with solutions, and is fastest with polymers having high molecular weight and low acid number;
- Opacity, which is controlled mainly through the selection of pigment and pigment particle size, can be increased by combining a low Mw solution in the grind with a hard (high Tg) emulsion in the let-down;
- Resolubility on the press can be increased by increasing either the acid number of the polymer or the ratio of solution to emulsion;
- Carry-up and transfer are greatest with polymers having relatively high Mw;
- Flow and levelling are best with high ratios of solution, while print sharpness, especially at high speed, is improved by higher ratios of emulsion;
- The greatest economy is achieved by formulating with very high Mw (high viscosity) solutions, which take large additions of water to effect their reduction to press viscosity.

Mr Wulf concluded his presentation by reviewing some of the principles of ink formulation and manufacture as they apply to aqueous systems, making these points:

- Millbase materials, millbase viscosity and dispersion time should be adjusted to give optimum results in terms of fineness of grind, transparency (or opacity) and economy;
- Efficient use of dispersion equipment usually demands a millbase of the highest pigment-to binder ratio that can be achieved, consistent with high throughput rates;
- The viscosity of aqueous systems is influenced by pH as well as by solvents;
- The choice of neutralizing agent is an important consideration. (Ammonia is fast-drying and fully volatile; slower amines give better pH stability both in manufacturing and on the press, but may retard drying or even plasticize the dried film; sodium ions produce a dried film that always remains water-sensitive, and may cause hydrolysis of some monomers.)

After a round of thoughtful questions and well-considered responses, Section Chairman Douglas Pratt commended Mr Wulf for his thorough coverage of a very timely topic, noting that water base technology is currently a subject of great interest in the ink industry.

Mr Pratt concluded the proceedings by wishing all members and guests a pleasant summer, and reminding them of the resumption of activities in the fall, beginning with the Section golf tournament in September.

J F Ambury ■

Natal Section

Joint meeting with the Corrosion Institute

An interesting joint meeting was held at the Hoy Park Recreation Club, Durban on 10 July 1990.

The topics and speakers were "Protective Coatings in Shipbuilding" by Mr Tim Henning and "New Technical Aspects of Surface Coatings in Shipbuilding" by Mr Mike Aldsworth.

Mr Henning covered the role of the paint department of a major shipbuilder and described the quality control, safety and application aspects as well as the overall project planning of painting from commencement of building. Because of fire hazards, coating systems with lower volatility and flammability are preferred. Careful supervision and accurate capturing of data was maintained at all times.

Mr Aldsworth discussed the very close liaison which exists between manufacturer and user. He discussed the application of new technology in respect of metal inert gas welding (MIGW) in comparison with the conventional welding. MIGW gives increased productivity but is more sensitive to the nature of the primer. The third generation inorganic zinc primers give far greater weld speed and less plate distortion when compared to the conventional polyamide epoxy primers.

Both speakers skillfully used slides to illustrate their lectures.

The vote of thanks was proposed by Mr Mike Eveleigh who commented on the complexity of shipbuilding and the need to "get it right first time". He then thanked International Paints for sponsoring the meeting.

E Puterman ■

Eighth annual one day symposium

The day-long Symposium on Past, Present and Future: A Review of the Surface Coatings Industry was held on 28 August 1990 at the Westville Country Club.

The programme and lecturers were the following:
Architectural Coatings-Mr P van der Walt
Heavy Duty Coatings-Mr M Eveleigh
Paint Manufacturing-Mr R John
Paint Application-Mr T Fanthorpe
Industrial Finishing -Mr R Johnson
Automotive Finishes-Mr E Els
Wood Finishing-Mr L Fisher

The concept was of great interest as it covered a wide spectrum of the Paint

Industry. The Symposium attracted a very good turnout and proved to be of benefit to the technicians and laboratory staff in the paint and allied industries.

An interesting comment was whether we are merely learning to use the old things better or are we really moving ahead with new technology.

After the Symposium a cocktail party, sponsored by Lewis and Everitt, was held and certificates of attendance were presented. *E Puterman* ∎

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