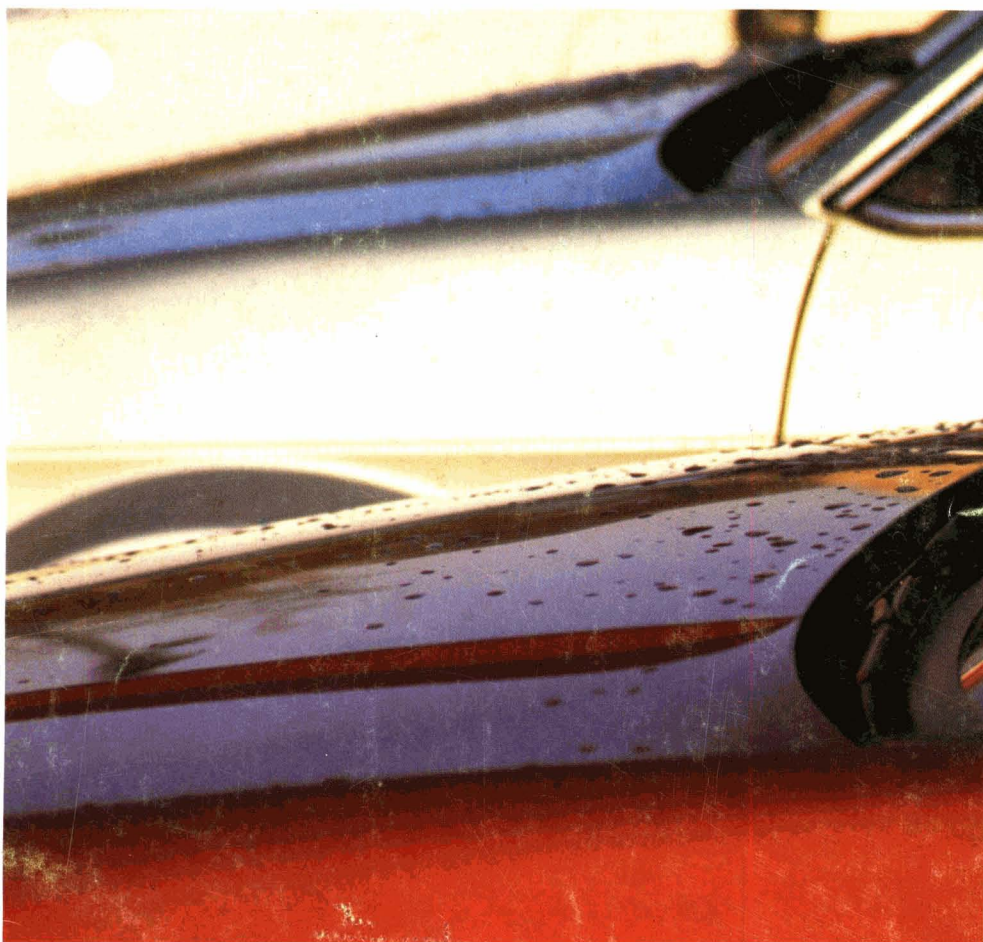




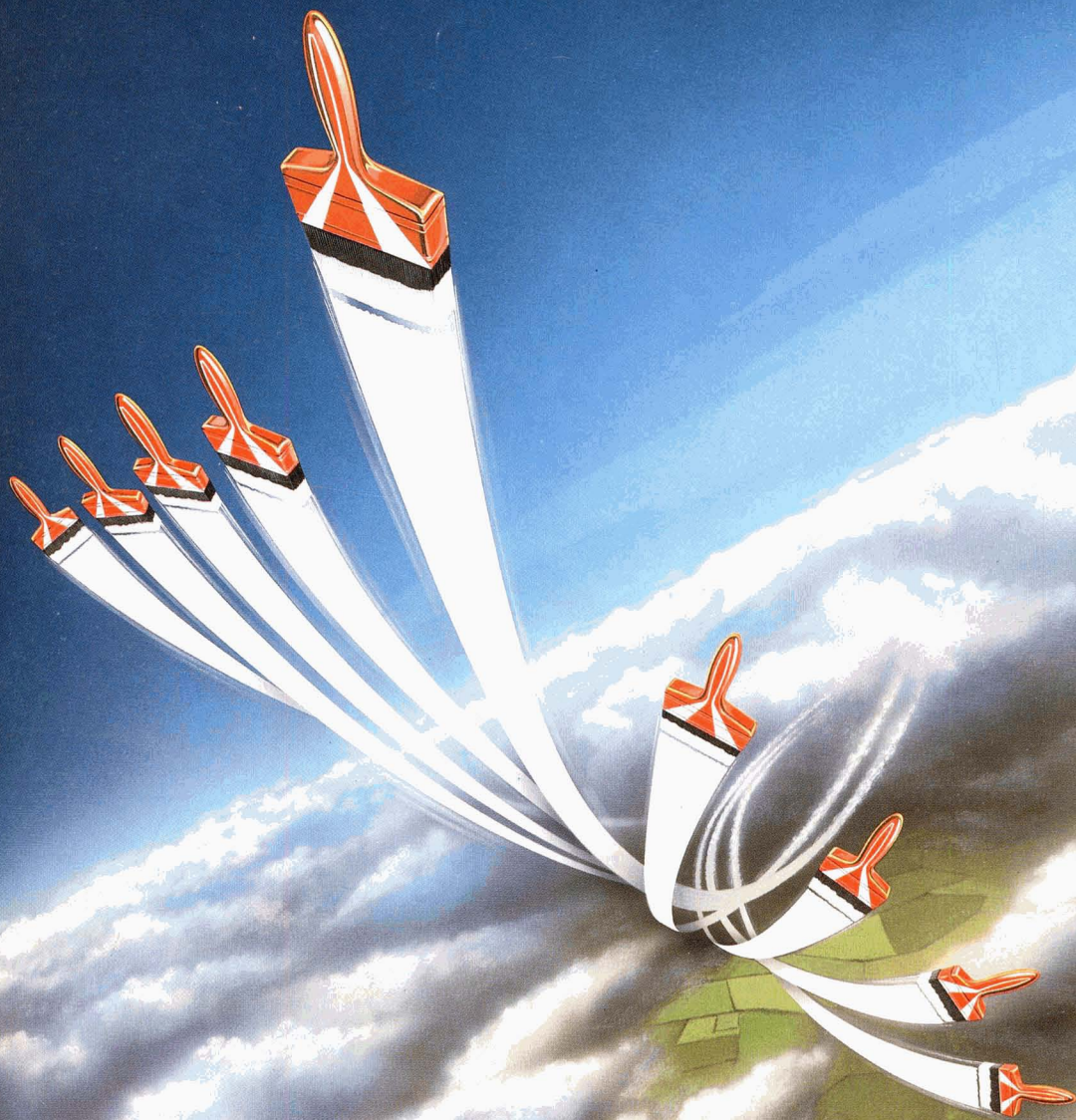
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Editorial correspondence should be addressed to the Hon Editor, *JOCCA*, and general correspondence addressed to the General Secretary at the Association Headquarters.

General Secretary:

C. Pacey-Day

Assistant Editor:

P. J. Fyne, MA, DPhil

Advertisement Manager:

F. Craik

Tel: 01-908 1086

Fax: 01-908 1219

Telex: 922670 (OCCA G)

Annual subscription to non-members: £75.00 (\$150), post free by surface mail, payable in advance.

Single copies £7.50 (\$15), post free by surface mail, payable in advance.

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Member of the
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Circulations



An Official Journal of the
Paintmakers' Association
of Great Britain Ltd.

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The front cover photograph shows the linking theme between Solsperse hyperdispersants and automotive paints. See page 310 for further information. Photograph courtesy of ICI Colours & Fine Chemicals.

Oil and Colour Chemists' Association

Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF England

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Printed by The Herald Press, Stratford-upon-Avon and 112 Bermondsey Street, London SE1 3TX. Tel: 01-378 1579.

OCTOBER

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OCCA CONFERENCE 1989

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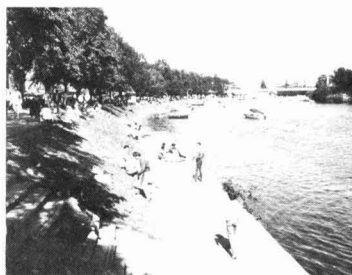
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For further information see the regular conference column in this issue on page 345.

SBPIM forecast price increase for UV/EB inks and varnishes

The Society of British Printing Ink Manufacturers Ltd report that a series of explosions during the last nine months at factories making acrylic acid has resulted in a serious shortage of this key material needed to produce the acrylates which are the basis of the monomers and polymers used in radiation curing products. There was already a shortage caused by an increased demand for chemicals based on acrylic acid and, as a result of these explosions, suppliers have now increased their prices with little prior warning to users. In order to ensure the continued supply of their UV/EB inks, varnishes and coatings to customers, printing ink manufacturers have little choice but to accept the increased cost of this vital raw material. This will inevitably mean that the prices of the inks and other products affected will also have to go up.

Magnesium Elektron boosts Zirconia production

Magnesium Elektron Ltd (MEL), the world's major producer of high purity zirconia and zirconium chemicals, is spending US\$30 million on modernisation and expansion of production facilities at Manchester in the United Kingdom and Flemington, New Jersey, in the USA. MEL, a division of Alcan Chemicals, has been manufacturing these materials for forty years. The combined capacity of the two plants, which is several thousand tonnes a year, will be increased by a third. At the Manchester plant the necessary planning consents have been obtained, the main contractor, Courtaulds Engineering, has been appointed and site work started. At the New Jersey plant, work is already well advanced implementing a process improvement plan which will increase production capacity.

Graco Korean deal

International fluids handling and finishing specialist Graco have been

awarded contracts worth £3.7 million by KIA Motors Corporation, Korea. The contracts are for the purchase and installation of a complete paint circulating system and a robotic finishing system at the KIA plant being built in Asan, 100 miles south of Seoul. Design and installation of the paint circulating system is being handled by Graco's Japanese subsidiary, Nihon Gray K.K.

Tioxide establishes Japanese subsidiary

Tioxide Group PLC, international titanium dioxide producer, has established a wholly owned subsidiary, Tioxide Japan K.K. This company with its own marketing and technical staff will develop a closer relationship with all its customers in Japan and provide a more integrated service. The Directors of the subsidiary will comprise: Messrs S. W. Elliott (Managing), D. M. Callow, J. R. Moody, J. R. Precious and E. Turton. Tioxide Japan K.K. will be capitalised at yen 95 million and based in Kobe.

PPG acquires Grow Group Inc

PPG have announced that the Grow Group will merge with a wholly-owned subsidiary of PPG. New York City-based Grow Group is a leading manufacturer of trade paints and chemical coatings, with annual sales of more than \$380 million. PPG Chairman Vincent A. Sarni said the transaction "will complement and strengthen the business of each entity. Grow Group will fit exceptionally well within PPG's Coatings and Resins Group."

Air Products Chief visits Anchor

Air Products Chairman and Chief Executive Officer, Dexter F. Baker, and President, Dr Bob Lovett, recently visited the main factory at Manchester of their company's new acquisition, the Anchor Chemical Group. Mr Baker commented: "Everything we have seen strengthens our belief that

together we can respond more quickly and effectively to customers' needs and accelerate the development of new products and markets." Anchor Chemicals Joint Managing Director, Dr Colin Tilley, confirmed that Air Products' epoxy additive business would be placed under the control of Anchor.

Rhône-Poulenc buys ICI silicones business

The Rhône-Poulenc Group, through its UK subsidiary, has reached an agreement with ICI for the acquisition of the ICI silicones business. This will expand the Group's product range within the international market.

Ellis & Everard PLC acquires United Chemicals

Ellis & Everard, the UK's largest independent chemical distributor, has acquired the business of United Chemicals, based in the US, for £21.2 million. United Chemicals is a major US chemical distributor covering Pennsylvania, Ohio, Virginia, Maryland, North Carolina and parts of adjacent states. The acquisition will double Ellis & Everard's existing US operations (the combined group has pro-forma sales of about \$170 million), making the enlarged group the sixth largest in the US chemical distribution industry.

Exxon Chemical expands MEK production

Exxon Chemical is investing \$5 million to increase the capacity of its methyl ethyl ketone (MEK) plant at Fawley, Hants, to 100,000 tonnes/year. The plant's present capacity of 90,000 tonnes/year is the largest in Europe. Exxon Chemical is currently building a new MEK plant in the US at Baton Rouge, Louisiana. Start-up of this 104,000 tonnes/year facility is planned for the fourth quarter of 1988.

Monsanto GmbH MF resins deal with Ernst Jäger

Monsanto GmbH, Düsseldorf,

has signed an agreement with Ernst Jäger Fabrik Chemischer Rohstoffe GmbH in Düsseldorf for the distribution of Monsanto's Resimene melamine formaldehyde resins. The Jäger company will sell the Resimene high solids resins in Germany, Switzerland, Holland Denmark through their existing sales organisation, together with their large range of synthetic resins. Besides the well-known high solids methylated, butylated and coetherified Resimene melamine crosslinkers, Jäger will also distribute the polyol modified types, the Modacure curing additive and the new PTSA and DDBSA acid blocked catalysts, free of amines, called Santocat.

Manders expands distribution

Manders plc has acquired decorators' merchants Deval of Northfields Ltd based in London and Ogden & Cleaver based in Luton. Roger Akers, Chief Executive of Manders, commented: "We will be opening a new ink depot at Luton following the closure of our Acton depot and this will then complete our two-year programme of improving our distribution through combined ink and paint branches."

Cray Valley are quality assured

Cray Valley Products Ltd has announced the Registration of its Resin Division at Machen, Gwent, South Wales, to BS5750 Part 2 1987. To meet the requirements of BS5750, all aspects of CVP business from the quality of raw materials purchased, through manufacturing and control techniques, to administration, product testing and despatch have been rigorously examined. Having met the required criteria, the ongoing audit and review process in the BS5750 Specification ensures that the quality and service provided by CVP will be maintained.

Chinghall Ltd 25th anniversary

Chinghall Ltd is this year celebrating its 25th anniversary as one of the country's top dispersion

manufacturers. The company has become recognised for its work in pioneering the widespread use of dispersions as clean, safe and cost effective alternatives to handling dusty and toxic materials. With the ever increasing pressure to provide a clean and hazard-free working environment, the handling of carbon black or other powders can cause many problems. By incorporating dusty powders in a suitable liquid, Chinghall produce either conventional paste dispersions, or free flowing granular dustless products – known as Clean Blends.

Best industrial museum

The Colour Museum in Gratton Rd, Bradford, has won the Unilver Award for the best industrial museum. The textile colour gallery is sponsored by the Society of Dyers and Colourists. The museum plans to expand into further uses of colour.

Products

New UF resin

BASF's D & P Division Plastopal H 73 IB is a new highly reactive urea-formaldehyde resin which contains little free formaldehyde and releases less formaldehyde in the curing process. Applications include acid curing lacquers and stoving finishes.

For further information Enter J101

New automotive in-mould coating system

Macpherson Industrial Coatings has made a breakthrough with their in-mould coatings for use with encapsulated glass windows. This new technology moulds a polyurethane gasket "in situ" by injecting RIM polyurethane around the glass at the production stage instead of fitting a separate gasket during car assembly, and a number of leading UK and overseas car manufacturers are currently investigating this production

technique. Derwent Plastics of Pickering are the first UK manufacturer to introduce this system with production of encapsulated window glass for the new Rover 800 fastback series. RIM Polyurethane used in this process needs a special paint coating to protect it from the effects of ultra-violet light and Derwent are using the latest technology from Macpherson Industrial Coatings with their Rimbond in-mould coating system.

Rimbond is catalysed and sprayed directly into the heated mould, and after only seconds of air-drying the polyurethane is injected into the mould. The result is a finish which is chemically bonded to the substrate as it forms an integral part of the moulding. This gives a very durable surface finish which vastly improves the abrasion, mechanical, and light stability properties of the polyurethane and which will not lose adhesion even under flexing. It is approved to Rover specification BLS 22 OF 15.

Macpherson Industrial Coatings have carried out a large programme of work on their Rimbond coatings and the materials are suitable for use with most leading polyurethane products including those from Dow, ICI, Bayer and BASF. In addition to the production of Rover windows, the process is also in use by Pilkington of Australia, and production trials are under way with many leading European car manufacturers. The paint system has recently been licensed to Glidden of the US.

For further information Enter J102

New intumescent coating from Granite

An intumescent flame retardant paint, Flamebloc, has been introduced by Granite Surface Coatings plc. Systems featuring the special purpose coating on a variety of substrates have been performance tested at the Warrington Fire Research Centre and were found to meet the requirements of a Class 0 fire rated surface, as defined in the latest Building Regulations. A non-toxic, water based, latex formulation,

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Flamebloc may be applied the same way as conventional paint, using a brush, roller or airless spray. It adheres strongly to timber, plywood, chipboard, plasterboard, cement render, concrete, brick and similar substrates, imparting additional fire resistance to combustible materials and maintaining the non-flammable properties of fire rated surfaces. The paint is not intended to withstand the intense heat of chemical or industrial conflagrations, but will prevent the spread of flame in many domestic, office or factory fires.

For further information Enter J103

New intumescent paint from Macpherson

The new improved intumescent fire retardant paint, TAF M112, from Macpherson Pearl Paints has just received Class 1 Spread Of Flame approval from the Warrington Fire Research Centre, after testing in accordance with BS 476 part 7, ie final flame spread < 165 mm. The new paint is effective in stopping the spread of fire across any surface on which it is painted. The paint may be used on a wide variety of wooden substrates. It may also be used on metal with a suitable primer. Decorative gloss 3592 from Macpherson Pearl Paints may be used as a third coat on chipboard with no loss of fire retardant properties.

For further information Enter J104

Equipment

Automated sample handling with particle sizers

Malvern has introduced the new PS15 Automatic Sample Handling Unit, designed for use with particle sizer analysers such as the Malvern Series 2600C instruments. The PS15 is designed for on-line or laboratory applications requiring dilution and dispersion of the slurry sample and it can be controlled either by computer or locally via the built-in



PS15 Automatic Sample Handling Unit.

soft-touch keypad. Separate input lines are provided for sample and diluting medium, the sample path being completely flushable to prevent carry over between measurements.

Programmable functions include duration and intensity of ultrasonic dispersion, amount of sample taken from the line or primary sampling system, stirrer speed and recirculation rate of the sample during measurement. A stainless steel flow cell with specially designed anti-reflection windows is provided for laser diffraction particle size measurements. Flushing of the complete system and background measurements on clean dispersant are also completely automatic. With this degree of control the dispersion and analysis can be tailored to precise requirements of the individual sample materials.

For further information Enter J105

New instrument for electrochemical

Applied Corrosion Monitoring Ltd has just launched a new Amstrad controlled product for the electrochemical paint evaluation and mass corrosion testing laboratories. It enables several electrodes to be polarised by an electrochemical AC or DC technique around the individual electrodes rest potentials at the same time in the same test cell. The individual response is then obtained from all the elements around their individual rest potentials. Frequently paint manufacturers need to evaluate painted samples by electrochemical techniques after environmental cabinet exposure tests. By using a 20 Channel

Offsetting Zero Resistance Ammeter it is now possible to immerse all 20 samples into the test tank at the same time, for the same length of time, before the electrochemical test is performed around the individual rest potential of all 20 samples. Thus all the samples are exposed to the same test conditions throughout the experiment which improves the statistical analysis and speed of testing.

For further information Enter J106

New Kontour electrostatic spraygun

The new Kontour Airmix automatic creates an adjustable spinning circular pattern of spray which slows up the forward speed of the paint particles from gun to the workpiece to give an enhanced wrap round effect. This improves the electrostatic spraying performance of materials with high resistivities and because of being assisted air, better penetration is achieved. The new Kontour automatic is easily removed from the electrostatic charging barrel for maintenance and servicing with minimum down-time and it is not necessary to remove the complete automatic spray gun from the system.

For further information Enter J107

Spectrum International developments in remote colour measurement

Spectrum International has available the Macbeth Eagle-Eye, the world's first automated colour surveillance system which precisely measures colour from four to twenty feet away. The Eagle-Eye installs out of the way of the production line allowing easy adjusting or servicing of on-line equipment. If production takes place under high temperatures or in harsh environments the Eagle-Eye can function efficiently behind glass. Advanced optics provides a high level of quality control with on-line calibration, long-distance accuracy and easy installation. The colour measurement system can handle surface irregularities as deep

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as half an inch. The Eagle-Eye Scanner Module can measure a three dimensional sample by focusing on different surface planes. It can scan a surface taking measurements at half second intervals. For a production line the Eagle-Eye focuses on the product from a distance and freezes the motion to sample the colour. The instrument illuminates the product with a pulsed Xenon light which can be directed at even the darkest colours and is unaffected by ambient light. The Eagle-Eye (EE) can be compared with conventional on-line colour systems (CC): Depth of focus = 0.5" EE, 0.1" CC; Area of measurement = 7.4" x 9.3" (8 ft) EE, 1" Φ CC; Distance illuminant to product = 4-20 ft EE, 1/4" CC; Optical geometry = Human Eye EE, 45°/0° optics CC. The instrument comes with a standard software package and custom software can be developed for special applications.

For further information Enter J108

3M oil sorbent test kits

A trial test kit of 3M Oil Sorbent is being offered free to anyone involved in tackling oil spills in industrial environments. Providing an ideal solution to oil containment, management and clearance problems, 3M Oil Sorbent is a specially formulated fibrous material able to absorb most types of oil upon contact. The kits comprise four types of oil, a sample of Oil Sorbent and a water tray for demonstration purposes. The sorbent is able to remove up to 25 times its own weight in oil and is completely reusable.

For further information Enter J109

Literature

New financial study of metal finishers

The new edition of the Financial Survey and Company Directory on "Metal Finishers" provides up-to-date information on over 650 companies within this sector. A three-year comparative study of six

key areas of company accounts are considered: turnover, pre-tax profits, total assets, current assets, current liabilities and directors' remuneration together with two calculated ratios: return on capital employed and profit margin. A directory section includes trading address, company secretary, holding company (if any), directors' names and principal activities, cost £185.

For further information Enter J110

Video test for handling of loose bulk materials

A new colourful A4 leaflet from vibration equipment manufacturers Triton Engineering Co Ltd outlines their no cost video-test service for the handling of loose bulk materials within the process industries. On receipt of customers' sample product, a video cassette film is produced showing vibration being applied to promote, for example, compaction, conveying, regular flow, uniform full spread feed and precise separations, etc., and is despatched back by return.

For further information Enter J110

Meetings

Adhesives

The Printing, Packaging and Papermaking Group of the Institute of Physics will hold a meeting on Adhesives on 8 December 1988 at 2 pm at the Institute's Headquarters, 47 Belgrave Square, London. Dr D. M. Brewis of Leicester Polytechnic will give a general introduction to the subject of surface analysis of bonded materials. There will also be speakers on the theory of adhesives, the methods of application and the testing of adhesive bonds. For further information call 01-235 6111.

COSHH

Details of the new COSHH regulations will be presented in a Sheffield University Risk Management Course on 13-14

December, 1988. For further details contact Mrs K. Wainwright on 0742 768653.

People

Vinamol appoint new General Sales Manager

Dr David Wilson has been appointed General Sales Manager for the UK and Eire of Vinamol Ltd. He takes up the post succeeding Chris Alderson-Smith, who has been appointed European Operations Director for the Speciality Polymers Division of National Starch. Since 1987 Dr Wilson has been European Business Development Manager for the paint and building industries at Vinamol. His new responsibilities will extend right across Vinamol's UK polymer emulsion business which includes the paint, adhesives, building, paper and textiles industries. Dr Wilson joined Vinamol in 1977 and has held posts as export marketing manager covering the Middle East, the Pacific Basin, Scandinavia and Eire. Earlier, he was technical manager for paint and building and, latterly, he has been UK sales manager for paint. Over the past eight years Dr Wilson has played a major part in accelerating the introduction of Vinamol's 'pressure polymers' to the paint industry.

BP Chemicals International appointments

Dr John G. Buchanan has been appointed a Director of BP Chemicals International and will assume responsibility for BPCI's specialities operations. John Turnbull and Doug Campbell have also been appointed Directors of BP Chemicals International.

New General Manager for Baxenden Specialities

The new General Manager of Baxenden's Speciality Chemicals Division is Dr Philip Morton, who joined Baxenden two years ago as Commercial Development Manager. The Baxenden Speciality Chemicals Division manufactures speciality isocyanates and engineering elastomers. The Division has developed moisture curing chemical building product intermediates, acrylic resins for UV coatings and gunnable sealants.

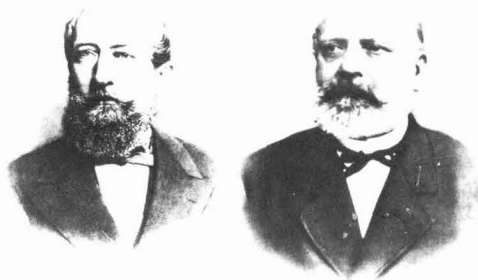
125 years of Bayer

Bayer, the chemicals-to-pharmaceuticals multinational marketing 10,000 different products and materials, celebrates its 125th anniversary. On 1 August 1863 dyestuffs merchant Friedrich Bayer (1825-1880) and the master dyer Friedrich Weskott (1821-1876) established the company Friedrich Bayer & Co in Barmen – now a part of Wuppertal – to produce and sell dyestuffs. The technique of producing dyestuffs from coal-tar derivatives had been discovered only a few years previously, opening up a whole new field for the still young chemical industry. Today Bayer's largest Sector, with 22 per cent of sales, manufactures chemicals such as Inorganics raw materials, Polyurethanes (a Bayer invention in 1937), and Coatings raw materials. The Organics Group specialises in intermediates for dyestuffs, engineering plastics, pharmaceuticals and rubber, among many industries. A communication centre and exhibition has recently opened in the Leverkusen, West Germany, headquarters. The exhibition illustrates the importance of Bayer products in everyday life and in particular features Healthcare, Nutrition, Leisure and Travel.

Since its foundation the company has registered nearly 150,000 patents and over 26,000 trademarks and today spends £650 million a year on research. Some 40 per cent of the company's sales come from new products developed in the last 15 years. Main areas of innovation for the next few years are now being intensified and include high performance polymers and advanced ceramics, new principles for pharmaceutical therapy and new diagnostic products, new crop protection systems, electronic photography and computerised typesetting. The good development of business over recent years, says an anniversary statement, has made it possible to expand capacity for the production of intermediate chemicals, for modern engineering plastics, and for starting products for polyurethanes. About 40 per cent of this investment is outside West Germany.

In the UK, the Bayer group employs 2,500 people and has a £550 million consolidated turnover. Bayer has been represented in the UK for 100 years. In fact 1991 is the 100th anniversary of the J. M. Steel

Company, at first an agency for Bayer product sales, then a part of Bayer. It subsequently changed its name to Bayer Chemicals Ltd and was a foundation company in the formation of the present Bayer UK Ltd in 1974.



Friedrich Bayer (left) and Friedrich Weskott.



The Leverkusen plant – headquarters of the company's central administration and the largest of Bayer's five production centres in West Germany. Some 37,000 people are employed on the 3.4 square kilometre site. It is one of the world's largest and most diversified production facilities for organic and inorganic chemicals, pharmaceuticals, dyestuff, polyurethane and rubber.



The polyurethane plant at the newest of Bayer's five production sites in West Germany.

Resins & Pigments 88

The eleventh Resins & Pigments Exhibition organised by PPCJ will be held at the Amsterdam Marriott Hotel on 9-10 November 1988. In conjunction with the exhibition the Paint Research Association/TNO will hold its 8th International Conference on "Optimising Paint Formulation: Preservation, Stabilisation and Cure" at the same venue on 7-9 November 1988. At the time of going to press the following companies have notified us (subject to the UK postal dispute) of what they will have on show at the exhibition:

Resins & Pigments 88 will be the first international exhibition with the new Akzo corporate identity to operate in a more market orientated structure. Within the **Chemical Division of Akzo** (Rm 217, 219, 221) a group has been formed to promote the wide range of Akzo chemicals for coatings applications. Among the products that can be discussed will be: Driers – full range of metal driers. Epoxy Curing Agents – complete range of water dilutable epoxy curing agents. Aluminium Silicates. Perchem Rheological Additives – comprehensive range of organoclay and hydrogenated castor oil thixotropes. Other products of interest will include Akzo additives such as peroxides for polyester putties, photoinitiators, adhesion promoters for plastisols, plasticisers.

For further information Enter J301

ARCO Chemical Europe Inc (Rm 355), a subsidiary of the ARCO Chemical Company, is one of the major producers of propylene oxide and its derivatives worldwide. A few years ago, ARCO started to produce ARCOSOLV® propylene glycol ethers and acetate solvents for the paints and coatings, printing ink and cleaner industries. It was proven in several independent toxicity studies that propylene based solvents are far less toxic than the traditional ethylene glycol ethers and acetates. Our stand personnel – Mr J. Roeser, Product Manager; Mr D. Penninck, Technical Manager and Mr R. Hin, Regional Manager Benelux – are looking forward to welcoming you during the exhibition.

For further information Enter J302

Baxenden Speciality Chemicals Division (Rm 310, 312) produces acrylic and urethane intermediates for a range of applications including the surface coating, adhesive and chemical building

product industries. Emphasis will be placed on these products latest developments in UV curable systems, cross-linking hot metal adhesives and the wide range of blocked urethanes available. Staff will be on hand to discuss the above applications, specific customer requirements and custom manufacturing facilities which include high temperature, fast throughput vacuum distillation facilities for temperature sensitive materials in addition to the capability of handling hazardous materials.

For further information Enter J303

Established specialists in amino coatings resins, **BIP Chemicals Ltd** (Edam Suite) has been developing its 'Beetle' range of butylated resins for many years. However, major advances made by the introduction of 'Beetle' methylated resins and their versatility has been further increased by developments in mixed ether resins. Some of the benefits which can be achieved with these resins will be demonstrated. Developments in saturated and rapid dry alkyds, supplementing the existing range of plasticising alkyds will also be shown. Sales and technical personnel will be in attendance.

For further information Enter J304

Blagden Industries Plc (Rm 302) are a European multi-national Group specialising in Packaging, Protective Equipment and Chemicals. The Chemical Division will be exhibiting data giving full information on the range of Alkyd Polyurethane, Silicone and Unsaturated Polyester Resins produced at their factory in Haverhill, England. Staff will be available for full discussions.

For further information Enter J305

Byk-Chemie GmbH (Rm 225, 227) will highlight tailor-made silicone additives, wetting and dispersing additives and defoamers for the coatings industry. Especially featured will be: The Disperbyk-160 family – the new generation of polymeric wetting and dispersing additives for inorganic and organic pigments and BYK®-310 silicone additive for decreasing the surface tension of paints and thus giving good anti-cratering properties, slip, substrate wetting.

The Product range of BYK® Labotron shown will include the gloss-meter family, especially the MICRO-GLOSS, the world's smallest gloss meter.

For further information Enter J306

The theme of the **Cray Valley** exhibit (Edam Suite, 1st Floor) will be "Cray Valley has the answers" . . . Cray Valley as innovators to the Industry will be emphasising new developments in environmentally friendly coatings, including radiation curing prepolymers; two pack acrylics; high solids decorative paints; acrylic and vinyl acetate emulsions; and a novel polyamide curing agent. With a world wide network of manufacturing bases and sales agencies, Cray Valley are well placed to serve the Industry in its 50th year of operation.

For further information Enter J307

Crosfield Chemicals (Rm 407, 409) will display its high performance and comprehensive range of HP200 Silicas which offer optimum matting efficiency and superb film smoothness in a wide variety of coatings applied to wood, metal or fabric. Crosfield's wide experience in this market allows for optimum selection from the HP range for accurate and consistent gloss control. For radiation curing systems Crosfield has developed HP39, which offers gloss reduction even in thicker coatings. In addition HP64 has been specifically designed for matting high clarity, low viscosity nitrocellulose systems. The use of Crosfield precipitated silicate pigments for extending titania in emulsion paints will also be displayed.

For further information Enter J308

Ernst Jager (Rm 403, 405) exhibit will feature highlights of Jagalyd – alkyd and epoxy ester resins, Jagapol – saturated polyester resins, Jagotex polymer resins and emulsions, Jagalux – UV curing resins, Bonosol – acrylic resins, Resimone – high solids and waterborne melamine resins of Monsanto. Exhibition Personnel include Heiko Schumacher, General Sales Manager; Bernd Schmitz and Petra Ungermann, Technical Staff; Siegfried Sternberg, Sales Representative of Jager Chemie Nederland. Ernst Jager is the worldwide representative of Union-Chemie, Dusseldorf.

For further information Enter J309

Goodyear Chemicals Europe (Rm 531, 533) will be featuring PLIOLOTE® and PLOWAY® Resins high performance binders destined to the paint industry produced in Le Havre, France. PLIOLOTE® resins are Styrene/Vinyltoluene acrylic copolymers which produce paints with excellent adhesion, water/alkali resistance, self cleaning and long lasting protection. They are used in exterior masonry coatings, anticorrosion paints, traffic, intumescent paints and waterproofing sealers. PLOWAY® is

the name of a new range of ecological resins soluble in virtually odourless, aromatic free solvents. Plioaway rheological resins are ideally suited for a complete range of low odour interior decorative finishes and high performance exterior masonry coatings. ® in this entry = Trademark, The Goodyear Tyre & Rubber Company, Akron, Ohio, USA.

For further information Enter J310

W. R. Grace & Co (Rm 234, 235), with headquarters in New York, is a multi-national company with prime interest in the field of speciality chemicals. Grace GmbH in Worms, Germany, is the European centre for the production of Micronised Silicas, Molecular Sieves, Cracking Catalysts and Silica Gel. "SYLOID" micronised Silicas are widely used as highly efficient matting agents in paints and lacquers. "SHIELDEX" an iron-exchange anti-corrosion pigment is finding increasing use as a non-toxic replacement for lead and chromate pigments. "SYLOSIV" micronised molecular sieve acts as a moisture scavenger in moisture sensitive systems.

For further information Enter J311

The **Heubach Group** will display this year its full palette of pigment products for the enamel and plastics industry. Zinc Oxides (French process), Zinc Dust pigment grade, chemical grade, chromium yellow, molybdate reds, Zinc Phosphates (Heucophos), high grade tailor-made pigments, Heucoflow pastes. Exhibition personnel will include Mr Noack, Authorized Manager; Mr Weigel, Authorized Sales Manager; Mr Schlüter, Product Manager; Mr Ellis, Sales Manager, Sales Office Benelux; and Mr Fischhofer, Sales Manager, Sales Office France.

For further information Enter J312

Hüls (Rm 423, 425) will be exhibiting crosslinking agents for powder coatings, epoxy curing agents, adhesion resins, ketone formaldehyde resins, saturated polyesters (VESTURIT®), vinyl chloride copolymers (VILIT®) and acrylic or styrene-butadiene copolymer emulsions (LIPATON®) as well as polyamide 12 fluidized-bed coating powders (VESTOSINT®).

The range of polyurethane materials include monomeric diisocyanates, polyisocyanates, PU resins and oxyesters. Of particular interest are the blocked isocyanates. PU system UB 893 BL is a combination of isophorone diisocyanate based blocked isocyanates and saturated polyester. The resulting system can be crosslinked at above 130°C using DBTL as a

catalyst, a primary use being in coil coatings.

For further information Enter J313

ICI Resins, the new group which integrates ICI's well-known product lines ALLOPRENE, HALOFLEX, LUMIFLON, WINNOFIL and the POLYVINYL CHEMIE products NEOCRYL and NEOREZ, will also exhibit the recently launched product lines NEOPAC, NEOTAC and NEORAD. NEOPAC are urethane-acrylic copolymers for parquet and other flooring applications (Architectural Paints). NEOTAC range of resins are for use in e.g. blister adhesives, cold seal adhesives, skin laminating and high performance Pressure Sensitive (Adhesives). NEORAD are products for waterbased UV-curing (Industrial Coatings). New polymers with improved chemical resistance for industrial woodfinishes and a new acrylic-alkyd copolymer for decorative paints with high gloss will be featured. The products will be shown in their different applications: Rm 507 - Industrial Coatings, Rm 509 - Architectural Paints, Rm 511 - Heavy Duty Coatings, Rm 515 - Ink, Paper and Adhesives.

For further information Enter J314

ISC Alloys (Rm 341) will recreate the atmosphere of a typical English Midlands pub in 'Ye Olde Rusty Bucket'. Visitors will be invited to sample traditional English beer and bar snacks and participate in pub games. Technical and commercial staff will be available as required to discuss ISC Alloys Zinc Dusts and Zinc Phosphate.

For further information Enter J315

King Industries exhibit (Rm 361) will feature speciality additives for high solids and water-borne coatings, including NA-CURE® and K-CURE® acid and blocked acid catalysts, K-FLEX® polyester polyols and urethane diols, K-Sperse™ dispersing agents and NACORR® rust and corrosion inhibitors. Emphasis will be placed on new products including K-Flex polyurethane diols for use as reactive diluents and polymer modification, and new K-SPERSE 152 dispersing agents which can be effectively used for organic and inorganic pigments in non-aqueous and solvent free compositions. Technical sales personnel on hand will include Dr Leonard J. Calbo and Ing Leen A. Stolk of King USA and Europe respectively.

For further information Enter J316

Lankro Chemicals Ltd (Rm 206/208) will feature a wide range of Photomer UV and EB curable oligomers and monomers. These materials are widely used in the ink, coatings, adhesive and

electronics industries. The range is composed of modified epoxy acrylates (Photomer 3000 series), polyester acrylates (Photomer 5000 series), urethane acrylates (Photomer 6000 series), new speciality oligomers (Photomer 7000 series) and low irritancy reactive diluents (Photomer 4000 series). Of particular interest will be the introduction of a new range of UV water-thinnable oligomers.

Polyurethane intermediates from Lankro's extensive range are used in such applications as coatings, primers, adhesives, binders, elastomers, sealants and pigment dispersants. Featured products and services will include Quasilan - liquid polyisocyanate prepolymers, Lankrothane - aqueous polyurethane latex, Estolan - polyester polyols, Propylan - polyester polyols, Propylane - polyether polyols and Polystab - speciality additives.

In the surfactants area, Lankro speciality emulsifiers for emulsion polymer production will be featured. These will include low foam anionic emulsifiers.

For further information Enter J317

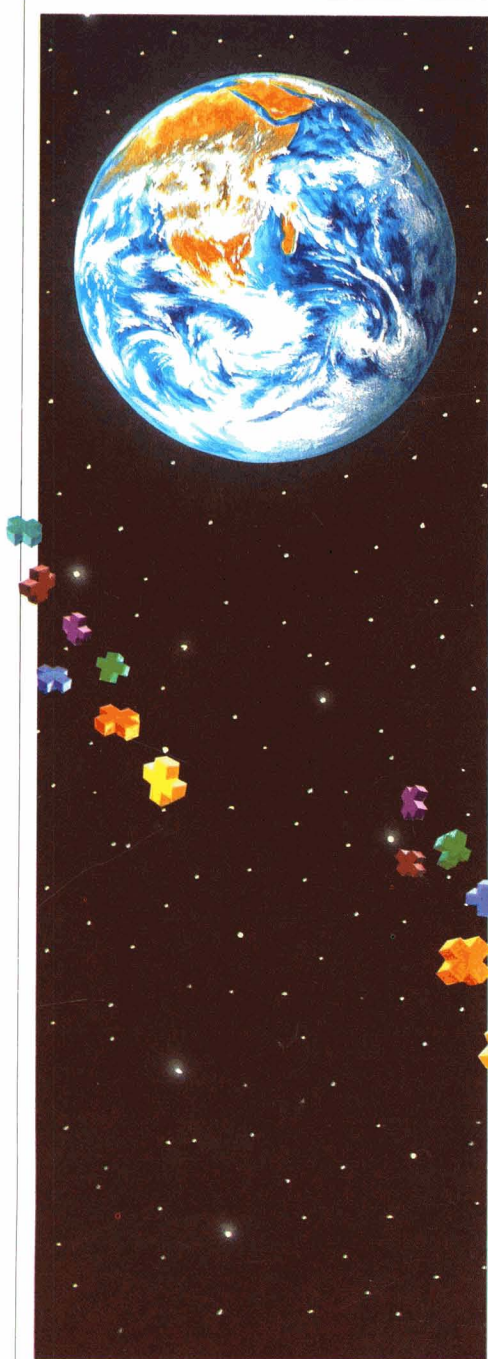
Leon Frenkel Ltd (Rm 257) is a privately owned, totally independent resin and printing ink varnish manufacturer located at Belvedere in Kent. Their current resin product range includes Ester Gums, Maleic Condensate Resins, Metallic Resinates, Rosin Modified Phenolics and various Alkyds. The company recently acquired the entire range of printing ink varnishes formerly produced by BASF, now produced and marketed under the trade prefix-ENNE to the same high standards established by BASF. Several new additions to this range will shortly be available. Commercial and Technical personnel experienced in both the UK and export markets will be available to answer any enquiries.

For further information Enter J318

The **Lubrizol Corporation** (Rm 539, 541), a speciality chemical company, serves the world market in transportation and diverse industries. The Diversified Products Group is a functional unit within the company designing and marketing chemical additives for applications in the paint, coatings and other industries. The product range includes rheology control agents, pigment dispersants, heat stabiliser components and corrosion inhibitors. Stand personnel include Mr P. Downing, Mr W. N. Hamilton, Mr D. L. Sheets, Mr G. Sterler and Mr J. Alalouf.

For further information Enter J319

Magnesium Elektron (Rm 308) will feature details on how zirconium



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compounds can be used to improve the adhesion of coatings to substrates, alter the rheology of coating polymers and improve the chemical and physical resistance of polymers used in the coatings, adhesives, non wovens and allied industries. Stand personnel will include Dr Peter Moles, Dr Ian McAlpine and Derek Brockis, who will be available to answer any technical questions that may arise.

For further information Enter J320

The resin company **Mitchanol International Ltd** (Rm 307, 309) will be at R & P showing specialist products for ink manufacturing: Mitchanol Transet Resins for gravure/offset; Surkyd Alkyds; Surkovar, Surkogel, Gelsol, Varnishes, Additives; Surkopak Polymers for packaging Flexo/gravure. New products include Transep MG Range resins for gravure, Mitchanol Hydrocarbon resins for gravure/offset and Surkopak X Urethane polymers for packaging flexo/gravure.

For further information Enter J321

Norwegian Talc (Rm 247, 249) offers a wide range of extenders, produced and graded according to strict quality specifications, for use in the paint and allied industries. These are known throughout the world under the brand name Micro Minerals, and include Microdol, Micro-Talc and Micro-Mica. Exhibition personnel will include Dr P. G. Leversen, Mr J. H. Venekamp, Mr O. Vogelpoel and Mrs R. Brodahl.

For further information Enter J322

Perstorp Polyols (Rm 532, 534) is one of the largest producers in the world of Pentaerythritol and Trimethylolpropane with plants in Sweden, the US and Italy. Perstorp also have speciality products like Allylethers and Alkoxyates for low-polluting coatings. Applications and know how will be available at R & P. Current development areas are radiation curing, waterborne and high solid systems. Further products are under development.

For further information Enter J323

The QUV Accelerated Weathering Tester will form the centrepiece of **Q-Panel Company's** display (Rm 229). This internationally accepted tester has now even greater versatility with the introduction, earlier this year, of the UV-A 340 Lamp. The UV-A 340 is the best available simulation of sunlight in the critical UV region between 365 nm and the solar cut-off of 295 nm. A wall chart indicating the spectral energy distribution of sunshine will be available on request. A selection of Q-Panels – reproducible steel and aluminium test surfaces for evaluating the performance

of applied coatings will be shown. Sample panels for evaluation purposes will be distributed. Q-Panel is represented in Holland by Kors BV, who will also be present.

For further information Enter J324

Schwegmann (Rm 216), West German manufacturer of paint additives, present a complete range of additives for the use in paints, varnishes, printing inks and similar coating systems. New products are "Blister Free 53" and "Blister Free 54". These silicone free de-aeration agents are mainly used in air drying, heat hardening and reactively curing paint and coating systems. Furthermore, Schwegmann offer new slip additives: Schwego Mar 8304 for solvent systems and Schwego Mar 8305 for water-soluble systems. Schwego Mar show a very good slip effect, give good levelling and improve the scratchability.

For further information Enter J325

The **SCM Chemicals Ltd** (Rm 331, 333) display will feature the launch of TIONA RCL-628, a new super durable chloride grade of titanium dioxide designed to combine long-life without compromising on opacity and gloss development. TIONA RCL-628 will be of special interest to manufacturers of such systems as coil coatings, aviation finishes, powder coatings, automotive coatings and transport finishes. SCM will also be featuring information on TIONA RCL-535, the multi-purpose chloride grade of titanium dioxide designed to reduce the number of grades needed to be stocked by manufacturers. TIONA RCL-535 has been proven in a wide range of aqueous and non-aqueous systems to provide the desired combination of opacity, gloss, colour, durability and stability required by discerning users. In addition personnel from both the technical and commercial departments will be on hand to discuss any questions you may have concerning the TIONA products.

For further information Enter J326

Silberline Ltd (Rm 347) will be exhibiting SILVET, a product range of sparkling silver-like aluminium flake pigments in non-dusting, granular form. Available in a wide range of pigment particle sizes, the flakes are immobilised in a carrier resin system, which has been selected for optimum compatibility with commonly used thermoplastics.

For further information Enter J327

Synthese BV [Akzo Coatings & Resins] (Rm 432, 434, 436) will highlight: For Coatings: a chip resistant primer for automotive applications, medium solids basecoat and

clearcoat/solid colour topcoat; resins modified with sag control agents; medium solids acrylic polyols for vehicle refinishing and industrial applications; developments in radiation curable products; waterbased products. For Printing Ink: the latest additions of UV-curable monomers and prepolymers, and our extensive range of hard resins for sheetfed and web offset inks. For the Adhesive Industry: waterbased and solventbased acrylic polymers for pressure sensitives; linear, branched, solvent free and solventbased polyester polyols for PU-adhesives; acrylic/methacrylic polymers for UV/EBC and (hydro) peroxide curable adhesives.

For further information Enter J328

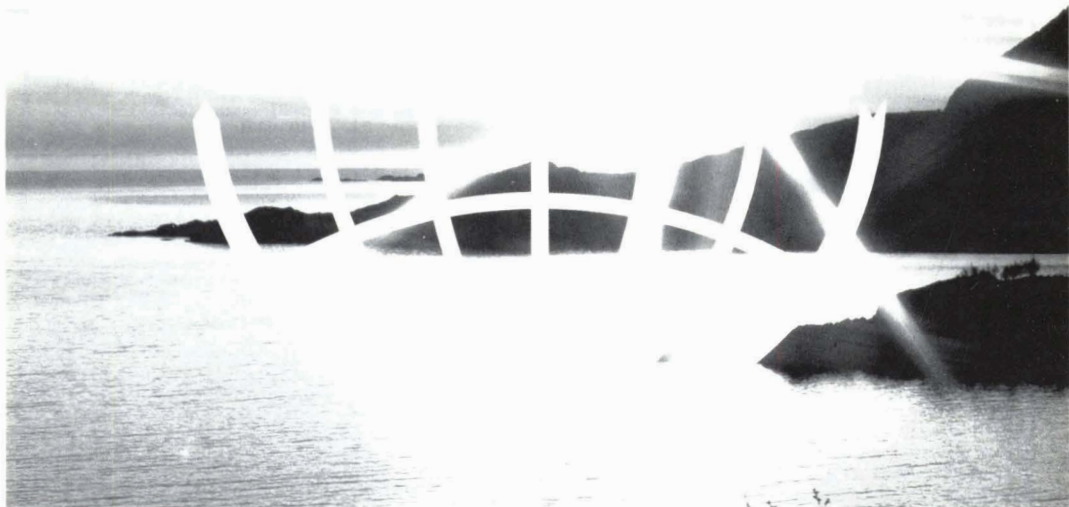
TDF Tiofine (Rm 236, 237) of the Netherlands has been producing TiO₂ pigments, using the sulphate process, for more than 25 years. The EC drafted standards for the waste levels of TiO₂ pigment plants and the Dutch government requires compliance with these standards by 1990.01.01. Tiofine will make a considerable contribution towards protection of the environment. The government approved its plan, which entails the investment of over Dfl 200 million, to build a new chloride process plant. This new plant will considerably relieve the environmental burden, have a nominal capacity of 45,000 tpa and be on stream in time.

For further information Enter J329

Tego Chemie Service GmbH of Essen, West Germany, supplies a range of additives and high temperature binders to the coatings industry. Of particular interest at this year's Resins and Pigment exhibition will be the introduction of a new additive TEGO® Glide 406, to give improved surface slip and mar resistance to coatings and inks. In addition two new defoamers TEGO® Foamex 800 and TEGO® Foamex 805 will be introduced for use in polyurethane emulsion systems.

For further information Enter J330

Tioxide Group PLC (Rm 321, 323, 325), the most international producer of titanium dioxide pigments, will be making the European launch of a significant new grade – TIOXIDE TR92. This has been designed to give superb dispersion, high stability and excellent optical properties and durability in the very wide range of media used in decorative and industrial paints. TIOXIDE TR92 is the most versatile quality grade of titanium dioxide currently on the market. Tioxide Group PLC will also be displaying its current investments plan for reducing environmental discharges. Exhibitions are tiring events to visit.



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For further information Enter J331

Union Carbide (Rm 443, 445, 447) will be exhibiting their range of coatings resins and resins intermediates. CYRACURE resins, diluents, flexibilizers and photoinitiators for cationic cure systems. Solvent and water based modified PHENOXIES for can and coil coating. UCARLNK low temperature crosslinker for water borne polymers. TONE caprolactone monomers and polyols producing high performance coatings for plastic and metal. SOLUTION VINYL RESINS for high performance coatings. A range of Speciality Solvents will also be exhibited.

For further information Enter J332

European polymer specialists **Vinamol** (Rm 106, 108) are presenting the latest in their range of 'pressure polymers'. These high-performance dispersions are supplied to customers throughout Europe from Vinamol's production site on the Dutch/German border. With excellent communication links to all major European centres, Vinamol offers a service to meet all requirements, from delivery to bulk to specialist batch production, right on the customer's doorstep. Products featured at this exhibition will include: Vinamol 3650, a multipurpose emulsion which gives high performance in tough, durable, water-resistant exterior coatings, and Vinamol 3267, an extremely versatile dispersion for fast setting adhesives with high wet tack.

For further information Enter J333

Wacker-Chemie GmbH (Rm 514, 516) supplies the paint industry with: Fumed Silica Wacker HDK (thickeners, thixotropic agents), silicone resins (binders), reactive silicone intermediates for copolymerisates, ethyl silicates (zinc-rich primers), paint additives (flow control), silicone masonry water repellents, varnishes and binders based on vinylacetate-vinylchloride copolymers or terpolymers as solid resins or dispersions (Vinnaps, Vinnol, Pioloform).

For further information Enter J334

Winter-Bouts BV (Rm 202, 204) is one of the leading producers of colour-systems in Europe. Winter-Bouts offer a range of systems: DIY market; machine tinting in injector systems; Professional market: Coltec Colourssystem (universal colourants); Industrial market: MPS system (multi-

purpose colourants); Inplant Tinting Systems. These systems are delivered exclusively to the paint industry. Winter-Bouts is represented by agents throughout Europe.

For further information Enter J335

Other companies exhibiting at Resins & Pigments 88 are:

Air Products, Chemicals Division European Group
Alcan Toyo Europe
Amoco Chemicals (Europe) SA
Bayer AG
Begvik Kemi AB
Berol Chemie BC
BP Chemicals International
Braive Instruments
Caldic Belgium NV
Gebroeders Cappella NV
Cera Chemie BV
Chemolimpep Hungarian Trading Co for Chemicals
Croda Resins Ltd
Daniel Products Company
Degussa AG
D E de Jong BV
Du Pont de Nemours International SA
Drew Industrial Division
DSM Resins BV
Dyno Cyanamid CV
Eastman Chemical International AG
ECC International Ltd
Eckart-Werke
Eka Chemicals BV
Engelhard
E & R Chemicals & Equipment BV
Ernstöm Mineral AB
Ferro
Finma Chemie GmbH
Floridiene
Fratelli Lamberti Spa
Frenkel Ltd
GAF Chemicals Corporation (Nederland)
Goodyear Chemicals Europe
Hendricks & Sommer Kunstharze GmbH
Henkel KGaA
Heybroek BV
Hitox Corporation
Hoechst Holland NV
Ich Zaanstad BV
ICI Colours and Fine Chemicals
IMA Instrument BV
Internatio-Alchemij BV
ISC Alloys Ltd
Kaerntner Montanindustrie
Kalkhof GmbH Petersen u Stroever KG
Kemira/Vuorikemia Division
Keyser & Mackay
Kirklees Chemicals
Dr Brundo Lange GmbH, Langer & Co
PVBA Corn Van Loocke Spri
Benda-Lutz Werke
Macheth Division of Killmorgen (UK) Ltd
Mearl International BV
E Merck
Micro Powders Inc
Minerals & Chemicals Assistance BV
Monsanto Europe SA
Münzing Chemie
Naintsch Mineralwerke Ges mbH Benelux
Necarbo BV
Nevin Polymers BV
NL Chemicals SA/NV
Nuodex Colourtrend BV
Nynas
Omya GmbH
Jan de Poorter BV
Procedes Farro SARL
J. Rettenmaier & Söhne GmbH & Co Inc
Rhenus BV
Rhöene-Poulenc
Rohm and Haas Company
RTZ Chemicals

Sachtleben Chemie GmbH
Sartomer International Inc
Schering Nederland BV
Carl Schlenk AG
W. O. C. Schöner GmbH
SCM Chemicals Ltd
Servo Delden BV
Shamrock Technologies SA
Sheen Instruments Ltd
SNZC Société Nouvelle des Couleurs
Zincoques
Strazdins PTY Ltd
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Thomas Swan & Co Ltd
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Verkaufsgesellschaft für Teererzeugnisse (VFT) mbH
Curt R. Vincentz Veriag
Wolstenholme Bronze Powders Ltd
Worlée Chemie GmbH
Zeelan Industries Inc.

For further information on the Exhibition contact: Joan Ridge, Resins & Pigments 88, Queensway House, 2 Queensway, Redhill, Surrey RH1 1QS, UK. Tel: 0737 768611. Tlx: 948669. Fax: 0737 761685.

For further information on the PRA/TNO Conference contact: Mrs Avril Henn, Conference Secretary, Paint Research Association, Waldegrave Road, Teddington, Middlesex TW11 8LD, UK. Tel: 01-977 4427. Tlx: 928720. Fax: 01-943 4705.

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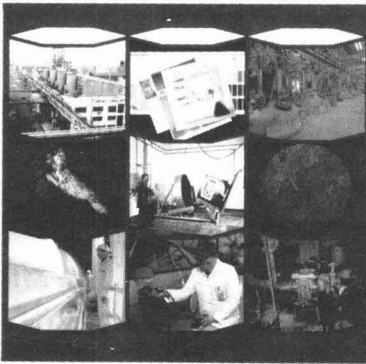
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Who needs wetting agents?

by A. C. D. Cowley and M. R. Gallon, Dispersants Group ICI Colours & Fine Chemicals, Hexagon House, Blackley, Manchester M9 3DA, UK

Introduction

In the past, the paint industry has had a general mistrust of additives such as wetting agents, and would only resort to their use to solve specific problems. And in many cases this view was justified. However, this attitude is gradually changing with the realisation that particular additives such as SOLSPERSE hyperdispersants will produce specific technical effects previously considered unattainable. Often these improvements in technical quality are achieved with a reduction in raw material costs.

Background

As one paint chemist put it: "If you know how to formulate paint, you don't need wetting agents." This view is commonly held in the paint industry, but how well does it stand up to the test? How often is thixotropy a serious problem when grinding millbases, resulting in low pigmentation and inadequate opacity in the finished paint? How frequently do millbases need to be given extra grinding in order to develop colour and gloss, particularly with coarse textured pigments?

It should be said that in most cases these problems are not due to any inadequacies of the paint formulator; they usually arise from the inherent deficiencies of the raw materials, particularly the resins in use. In traditional paint millbases, the pigments are ground in a bead mill or in other attrition equipment, and as the pigment agglomerates are broken down and separated it is the function of the resin to wet-out the pigment surface and form a stabilised dispersion of the pigment in the medium.

The efficiency of this dispersion process is to a large extent

controlled by the nature of the medium and is therefore limited by the wetting properties of the resin in question. Usually the resins are designed primarily to give good film properties, e.g. adhesion, toughness, chemical resistance or good durability on exposure, i.e. good film integrity, gloss retention, etc. It is rare for the resin to have been designed specifically to give good pigment wetting properties, so it is not surprising when these problems are manifested.

The role of wetting agents

Over the years paint formulators have tried to overcome these problems by utilising wetting agents to form stable dispersions, but the results have not always been satisfactory. This is not surprising as the products evaluated as wetting agents in solvent-based paints are often ineffective for the following reasons:

- (a) The use of single wetting agents ignores the wide differences in surface chemistry of pigments and as a result those agents that may be effective on inorganic pigments (polar surfaces) are usually ineffective on organic pigments (non-polar surfaces).
- (b) The wetting agents are often derived from natural vegetable oils and therefore contain a maximum of 18 carbon atoms which is too short a chain length to produce an effective steric barrier around the dispersed pigment particle.
- (c) The amount of wetting agent used is arbitrarily determined. Wetting agents have often been recommended for use on a weight basis, e.g. 1-2% on weight of paint, instead of considering the surface areas of the pigments to be wet-out. A consequence of using an excess of a wetting agent is that it cannot all

be anchored to the pigment and may be free to migrate to the surface of the coating resulting in loss of gloss and heavy dirt pick-up. By contrast, inadequate use of wetting agents may result in an incomplete steric barrier around the pigment particles which can result in a viscosity rise on storage of the paint, or in severe cases, aggregation of the pigment particles.

Due to these inadequacies, the use of traditional wetting agents is often only as a last resort, in order to solve a particular dispersion problem.

The development of hyperdispersants

As a result of the need to achieve better dispersion and stabilisation of pigments in solvent-based systems, ICI Colours and Fine Chemicals used novel and more powerful chemistry to develop a unique range of dispersing aids known as Solspers hyperdispersants.

The hyperdispersants are based on a two-part structure which comprises an anchoring functional group attached to a polymeric solvatable chain, and it is the particular combination of these which leads to their effectiveness. Efficient adsorption of a hyperdispersant on to a pigment surface can only occur if there is a strong interaction between the anchor group and the pigment particle. Obviously a single type of anchor group will not react with all types of pigment surfaces and hence a variety of anchor groups is needed for the wide range of pigments (e.g. titanium dioxide, phthalocyanine blues, carbon blacks) currently used in paints.

For efficient steric stabilisation the hyperdispersant must have polymeric chains which are compatible with the medium and be of sufficient length to provide an effective steric barrier to counteract the attractive forces between the particles. The molecular weight or chain length must be optimised: if it is too short, poor steric stability is obtained, if it is too long, it could

fold back on to the pigment thereby compressing the steric barrier, leading to re-aggregation. The chemistry of the polymeric chains can be modified to improve compatibility and solubility in solvents of different polarity, and the selection of the optimum Solsperse hyperdispersant is usually determined by the solvents present in the finished paint.

Hyperdispersants should not be confused with the more familiar wetting agents or surfactants – they are quite different. Unlike surfactants, hyperdispersants will not emulsify two liquids. Another more relevant difference arises due to the design of the hyperdispersants. As they are of much higher molecular weight than classical surfactants, they are more inert and when used in traditional paint systems, they have no adverse effect on durability. Indeed, in many applications such as automotive finishes, durability has been enhanced when Solsperse hyperdispersants have been used.

Solsperse 24000 for industrial paints

Most industrial stoving and chemically-cured finishes are based on resins soluble in aromatic hydrocarbons, esters or ketone solvents. Solsperse 24000 was designed specifically for these systems having good compatibility with solvents of intermediate polarity. Solsperse 24000 is particularly efficient for wetting out inorganic pigments which have high polarity, e.g. titanium dioxide, iron oxides and other pigments and extenders containing heavy metals. It becomes firmly attached to the inorganic pigment surface by an ion-pair bonding mechanism. Solsperse 24000 has multiple anchor groups, each of which can form a weak bond with organic pigments, and the overall effect is to give strong adsorption to these pigments also.

In the case of heavily surface-treated pigments such as the flocculation resistant phthalocyanine blues, or the high surface area channel black pigments, adsorption can be enhanced by using the synergist hyperdispersant,

Solsperse 5000, which is based on a copper phthalocyanine derivative containing polar groups. When Solsperse 5000 is incorporated into millbases containing phthalocyanine pigments, since the two products are physico-chemically similar, strong adsorption results due to Van der Waals' forces. The Solsperse 5000 is adsorbed on to the pigment and produces a more polar surface on to which the Solsperse 24000 can be adsorbed.

Solsperse 22000 is a second synergist, used less frequently in industrial paints. It can enhance the performance of Solsperse 24000 when used with organic yellow pigments and yellow-shade red pigments.

Thus by using Solsperse 24000 alone or a blend with a synergist, pigments of widely differing surface polarity can be effectively wet-out, producing very stable dispersions. This exceptional versatility is one reason why Solsperse 24000 is increasingly preferred by producers of industrial paints over competitive products.

Optimising the dispersion process

If the dispersion process is not carried out efficiently the resulting dispersion will be of poor quality and may manifest such imperfections as poor rheology (thixotropy), unsatisfactory fineness of grind, haziness or low gloss, or inadequate flocculation resistance.

On the other hand, if pigments are dispersed and stabilised efficiently, the resulting dispersions will have higher colour value or intensity, cleaner/brighter shades and, in the case of fine particle sized pigments, high transparency. Paints made from these dispersions will exhibit better viscosity stability particularly on storage, excellent gloss and flocculation resistance and less colour change on exposure to weathering.

It is therefore important to optimise the dispersion process and to use hyperdispersants efficiently in order to ensure that high quality paints are produced.

When Solsperse 24000 is used in industrial paint millbases, the

objective is to wet-out the pigment surface and ideally create a mono-molecular layer around the pigment, thereby preventing other pigment particles from approaching too closely. In order to produce a mono-molecular layer on the pigment surface it is necessary to use up to 2 mg of Solsperse 24000 per square metre of pigment surface. Thus for inorganic pigments with low surface-areas of say 10 m²/g up to 2% Solsperse 24000 on pigment weight are needed, whereas a finer particle size organic pigment with a higher surface-area of say 50 m²/g will require 10% Solsperse 24000 on weight of pigment.

When Solsperse 24000 is incorporated into a paint millbase one of the more obvious effects is on the millbase rheology. As the hyperdispersant is adsorbed on to the pigment surface, the particle-particle interactions are reduced and the millbase becomes more fluid and thixotropy decreases. Usually the viscosity falls to a minimum level when the amount of hyperdispersant is just sufficient to produce a complete mono-molecular layer around the pigment. It is possible to correlate the drop in viscosity, with the concentration of hyperdispersant in the millbase. In fact one can use these viscosity measurements to determine the quantity of hyperdispersant to use in the absence of reliable data on the surface-areas of pigments or extenders.

In millbase formulations where several types of pigments are to be dispersed as a co-grind, the amount of hyperdispersant required is simply the sum of the amounts needed for each pigment (related to its surface area). Consider the Solsperse 24000 requirement for a co-grind containing a 10:1 blend of titanium dioxide:carbon black as shown in Table 1. A co-grind formulation containing 11 grams of pigment would require 0.4 g of Solsperse 24000 to satisfy the surface-area requirements of the pigment. This example demonstrates the need to consider the surface-area of all pigments and extenders in formulation, particularly if the minor

Table 1

	Pigment (g)	Surface-Area (m ² /g)	Total Surface-Area (m ²)	Solsperse 24000 required at 2 mg/m ²
"White"	10	10	100	0.2 g
"Black"	1	100	100	0.2 g

components are organic pigments of high surface-area.

As Solsperse hyperdispersants have a dramatic effect on millbase rheology it is essential to monitor the viscosity of the millbase during the dispersion process. If it is found that the viscosity has dropped to an unacceptable extent (i.e. inadequate shear conditions) the pigment content in the millbase should be increased. This adjustment to the original formulation will not only improve the efficiency of the dispersion, but it will produce a bonus on increased productivity, i.e. more paint can be made from a given mill. This feature is particularly attractive if milling capacity is limited, obviating the need for capital investment in new mills.

Method of use of Solsperse 24000

It is well known that the rate of reaction of two chemicals is directly proportional to the surface areas coming into contact. By analogy, the rate of wetting-out of the pigment is directly related to the contact between the hyperdispersant and the pigment surface.

An efficient method of ensuring maximum contact between the pigment and Solsperse 24000 is to dissolve the latter in the grinding vehicle, before any pigment is added. Solsperse 24000 is supplied in a non-dusty solid physical form to allow users maximum flexibility and to avoid the costs associated with transport of solvent. It is sometimes more convenient to make up a 25% stock solution in a suitable solvent, so that it is always available when required for addition to the millbase. In the millbase, the hyperdispersant will be competing against the resin in the grinding vehicle for the pigment surface. Therefore to obtain maximum effect from the

hyperdispersant it is preferable to minimise the amount of resin present in the millbase.

In fact it is possible to use Solsperse hyperdispersants to produce stable dispersions in solvent alone, such is the effectiveness of their stabilisation. This effect can be utilised to advantage in the production of wood stains, which are required to be free of resin. However, for most paints this technique is not practical since in the absence of some resin in the millbase, there is a risk of shock-seeding the dispersion when highly viscous or concentrated resins are added to let-down 'solvent-only' dispersions.

A more practical approach is to carry out the dispersions using grinding vehicles of 10% resin solids content. The presence of the resin helps to encapsulate the pigment/hyperdispersant dispersion and prevent shock-seeding. The attraction of using a low resin solids grinding vehicle in the millbase is that its viscosity will be lower than in conventional grinding vehicles, with the consequence that higher pigment levels can be incorporated (greater productivity) without exceeding the required millbase viscosity. In addition, by increasing pigment content and reducing resin content, Solsperse 24000 offers the possibility of making highly versatile dispersions that can be let-down with a variety of resins.

The order of addition of components to a millbase is important. The resin and solvent should be added first, followed by the Solsperse 24000, or preferably the solution of Solsperse 24000. When this mixture is homogeneous, the pigment may be added in stages. The premix or milling viscosity should be monitored to ensure that it is at an acceptable

level. If adjustments are necessary to modify the viscosity, it is essential to maintain the correct ratio of Solsperse 24000:pigment in order to satisfy the surface-area requirement of the pigment.

The effectiveness of Solsperse 24000 in wetting-out pigments can be measured in terms of the milling time required to obtain a satisfactory dispersion. Dwell times can often be reduced by 20-30%.

These millbase dispersions can be let-down in the conventional manner, preferably using agitation when the resin solutions are added. The higher pigment loadings in the millbases containing Solsperse allow greater flexibility in formulating the final paints. This is particularly useful when producing high solids paint (low VOC) or where higher opacity finishes are required at conventional viscosity.

Some of the benefits of utilising Solsperse 24000 in industrial paint millbases can be seen in the following examples.

Example 1 - Titanium Dioxide

In conventional millbases for bead milling, the pigment content is usually about 65% by weight, and the grinding vehicle can have a non-volatile content between 20% and 50%.

If Solsperse 24000 is added to these millbases, the hyperdispersant wets-out the pigment and reduces the viscosity of the millbase. This allows an increase in pigment content over conventional millbases. Indeed, in order to create sufficient shear, it is essential to raise the viscosity of the millbase by increasing the pigment content. Successful millbases incorporating Solsperse 24000 typically have pigment contents in the range 78-80% (see Table 2). As such large quantities of titanium dioxide have to be wet-out by a small quantity of hyperdispersant, it is necessary to pre-dissolve the Solsperse 24000 in the grinding vehicle before adding the pigment.

The main attraction of the hyperdispersant formulation is the higher

Table 2

Bead Mill Formulation	Conventional millbase (%)	Solsperse millbase (%)
40% resin solids solution	35	—
10% resin solids solution	—	19.0
Solsperse 24000	—	1.0
Tioxide RCR2 or TR92 (Tioxide)	65	80

Table 3

Ball Mill Formulation	Conventional millbase (%)	Solsperse millbase (%)
20% resin solids solution	70	—
10% resin solids solution	—	58.7
Solsperse 24000	—	6.3
Sicotrans Red L2817 (BASF)	30	35

Table 4a

%Solsperse 24000 on quinacridone violet						
	0	6	10	15	18	22
d Str	Control	0	1.1	1.7	1.5	1.2
d Floc	3.2	2.3	2.0	1.5	1.8	1.9

pigment content in the millbase which results in greater productivity from a given mill, and a lower unit production cost. For high volume lines, such as titanium dioxide bases, this reduction in processing costs can be of considerable benefit. If plant capacity is fully occupied with conventional millbases, the Solsperse formulation can be used to produce greater output or to free plant for other millbases. In addition, customers report that paint films containing Solsperse 24000 have superior gloss and distinctness of image.

Example 2 – Transparent Iron Oxides

Transparent iron oxides are finding increasing use in a wide range of surface coatings from wood finishes to automotive paints. They are attractive in colour and have excellent durability, but they have a relatively hard texture which makes them difficult to disperse. Most of their applications demand high transparency and so millbases containing these pigments often require prolonged milling periods.

Transparent red iron oxides tend to have high surface areas, typically 85-90 m²/g. In order to satisfy this surface it is necessary to use 2 mg of Solsperse 24000 per square metre, or 18% hyperdispersant on weight of pigment (see Table 3).

Solsperse 24000 can be used to good effect with these pigments. It will wet-out the surface of the iron oxide very rapidly and assist in the dispersion process resulting in a faster rate of transparency development and a reduction in milling times by as much as 30-50%.

Example 3 – Organic Red Pigments

3.1 Quinacridones (Table 4)

With fine particle size pigments such as quinacridones it makes economic sense to wet-out the pigment surface effectively in order to develop full tinctorial strength and to minimise any tendency to flocculate.

The amount of hyperdispersant required depends on the surface-area of the quinacridone when fully

dispersed. This may be determined by preparing a series of millbases with increasing amounts of Solsperse 24000 on weight of pigment (see Table 4a). When the hyperdispersant is added in increasing quantities, the viscosity of the dispersed millbase falls to a minimum level, and the millbase with the lowest viscosity has been found to have the optimum ratio of hyperdispersant to pigment. In this series the resulting millbases were measured for viscosity and it was found that the use of 15% Solsperse 24000 on weight of quinacridone violet produced the lowest viscosity. To assess whether this was the optimum, paints were made up and assessed for tinctorial strength (d Str), against a control with no hyperdispersant. The degree of flocculation was also assessed measuring the total colour difference (d Floc) between the sprayed paint and a pour down. This series of millings confirms that the tinctorial strength is maximised and the degree of flocculation is minimised when the optimum ratio of hyperdispersant to pigment is used. By developing 20% high tinctorial strength (d Str=1.7) compared with the control formulation, it is possible to reduce the organic pigment content in the paint and so cut pigment costs (see Table 4b).

3.2 Perylenes (Table 5)

Perylene red and maroon pigments are commonly used in full shade applications to give opaque or, particularly, transparent shades depending on their particle size distribution. The pigments tend to have high oil absorptions and high surface-areas and this limits the amount of pigment which can be incorporated into a millbase.

By incorporating Solsperse 24000 or Solsperse 24000 with Solsperse 22000, it is usually possible to obtain much higher pigment loadings in the millbase without exceeding the conventional viscosity limits, giving rise to greater formulating flexibility in the finished paints. Combining Solsperse 24000 with the synergist may be necessary with only the most difficult pigments. As higher

Table 4b

Ball Mill Formulation	Conventional millbase (%)	Solsperse millbase (%)
20% resin solids solution	82.5	—
10% resin solids solution	—	71.2
Solsperse 24000	—	3.8
Monolite Violet 4R	17.5	25

Table 5

Ball Mill Formulation	Conventional millbases (%)		Solsperse millbases (%)	
20% resin solids solution	80	80	—	—
10% resin solids solution	—	—	59.7	70
Solsperse 24000	—	—	5.3	4.5
Solsperse 22000	—	—	—	0.5
Paliogen Maroon L3920 (BASF)	20	—	35	—
Hostaperm Red P2GL (Hoechst)	—	20	—	25

Table 6

Ball Mill Formulation	Conventional millbases (%)		Solsperse millbases (%)	
20% resin solids solution	80	80	—	—
10% resin solids solution	—	—	63.2	64
Solsperse 24000	—	—	1.8	6
Novoperm Red F2RK70 (Hoechst)	20	—	35	—
Monolite Red 2Y	—	20	—	30

loadings of the perylene pigment are used in the millbase, less plant capacity is occupied giving rise to lower processing costs and scope for greater productivity. In addition, better dispersion of the pigment is often seen leading to improved intensity and transparency.

3.3 Other Red Pigments (Table 6)

Pigment Red 170 is increasingly used in full shade to replace lead chrome pigments because of its high opacity and good fastness properties. Solsperse 24000 is again extremely effective in allowing dispersion at increased pigment content. Its use also leads to an improved dispersion quality and paints with increased intensity and brightness.

Pigment Red 168 (dibromoan-

thanthrone) is important as a shading component in many high performance coatings due to its unusual shade and its excellent brightness and durability. Solsperse 24000 increases the tinting strength of the pigment and reduces the cost of formulations.

Example 4 – High Surface-Area Carbon Blacks (Table 7)

There is a vast range of carbon blacks on the market, and for simplicity, these can be split into two groups. The tinting grades usually have relatively low surface-areas up to 150 m²/g, whereas for full shade or mass-tone blacks, the surface-areas may be as high as 500 m²/g. As a general rule, the use of 2 mg hyperdispersant per square metre of pigment surface should be sufficient to wet-out the pigment

with a mono-molecular layer.

Thus in the case of some channel blacks which have a surface area of 500 m²/g it is necessary to use 100% of hyperdispersant on weight of pigment. While this appears to be a high level of hyperdispersant, finished paints contain very low pigment concentrations (say, 2.5%) and the ratio of hyperdispersant to total non-volatile vehicle is correspondingly low. As a consequence no adverse effects on durability would be expected and recent trials in production of automotive finishes have shown excellent durability and gloss retention on exposure.

The use of Solsperse 24000 or Solsperse 24000 with Solsperse 5000

Continued on p329

The influence of associative thickeners on coating performance.

Part IV: Formulation surfactant effects

by T Murakami, R. H. Fernando and J. E. Glass, Polymers and Coatings Department, North Dakota State University, Fargo, North Dakota 58105, USA

Abstract

The effect of anionic and nonionic formulation surfactants with different critical micellar concentrations (CMCs) on the properties of coatings containing associative thickeners is discussed. Variations in coatings rheology, sag, gloss and scrub resistance are reported. In addition, the influence of associative thickeners on syneresis and pigment settling is observed. The small particle-size, all-acrylic latex employed in previous parts of this series is the binder in this study.

The rheological variances are related to the CMC of the surfactant, not to its nonionic or anionic hydrophilic group. Higher viscosities at low shear rates and lower viscosities at high shear rates are observed when the formulation surfactant is very hydrophobic and the associative thickener is a styrene/maleic acid terpolymer (SMAT). The hydrophobic formulation surfactant does not effect a dramatic increase in low shear viscosities with the HEUR type associative thickeners. Dramatically lower high shear viscosities are observed with the most hydrophobic surfactant except in formulations thickened with HEUR 200. The rheological responses of coatings thickened with HEUR 200 are distinctly different from that of other associative thickeners with variation of the formulation surfactant's CMC. This is consistent with HEUR deviations in previous studies. Differences in film scrub resistance among thickener/surfactant pairs are observed in 57 PVC formulations. As the concentration of thickener is increased, the scrub resistance is decreased in all systems. A similar trend is evident as the hydrophilicity of the surfactant increases. Formulations thickened with the lowest molecular weight associative thickener, HEUR 100 resulted in films with very poor scrub resistance.

Significant pigment settling is observed only in SMAT (the only ionic thickener used in this study) formulations. Parallel studies of SMAT coatings without the extender pigments do not exhibit settling.

Introduction

In the previous parts of this series¹⁻³, the influence of hydrophobically-modified, water-soluble polymers (H-M, W-SPs) on the rheological performance of coating formulations varying in PVC and %NVV was investigated. In Part I¹ a small-particle (number average diameter - 117 nm), all-acrylic latex was employed as the binder of an interior water-borne latex formulation; in Part II² a large-particle, (number average diameter - 347 nm) heterodispersed vinyl acetate / acrylate latex was employed. The latter latex was stabilized in part by hydroxyethyl cellulose, chemically bound to the surface of the latex⁴. In both studies, coating formulations were prepared by varying the amount of an associative thickener (i.e., H-M, W-SPs) or hydroxyethyl cellulose (HEC) to achieve different Stormer viscosities (measured in Kreh units, (KU)). Pigment volume concentrations (PVCs) of the formulations were varied by controlling the amounts of extender pigments. Extreme differences in rheological performance among associative thickeners were observed with a given latex as a result of PVC variations. For most associative thickeners significant variations in rheology and thickening efficiencies were observed between the formulations containing the two latices at a given PVC. Some thickeners (e.g., HEUR 200 and SMAT) exhibited a reversal in performance with latex variation. The exceptions were HEUR 708 and HEC which showed little sensitivity to formulation changes.

In both Parts I and II, the total percent nonvolatiles by volume (%NVV) of the formulations was 32. In Part III³ the effect of variation in %NVV was examined in formulations containing the two latices described above. By controlling the amount of water in the formulation, %NVV was varied at 22, 32 and 42, while varying the PVC at 25, 35, 45 and 57 at each %NVV level.

Two parameters, high-and-low-shear viscosity efficiency factors (ϵ_h and ϵ_l), were defined to facilitate data analysis; both ϵ_h and ϵ_l increased as the %NVV level increased, but were insensitive to PVC variations at 22 and 32 %NVV. At 42 %NVV a notable dependence of ϵ_l on variation in formulation PVC level was observed in the small-particle, all-acrylic formulations; it increased as the PVC decreased indicating flocculation of latex particles. Both ϵ_l and ϵ_h were dependent on PVC at the 42 %NVV level in formulations containing the larger, HEC-stabilized latex. Unlike the small all-acrylic formulations, both parameters decreased as the PVC decreased in the HEC-stabilized latex formulations. In addition to these differences, the studies again emphasized the variations in rheological performance among the H-M, W-SPs and suggested differences among their thickening mechanisms with a given latex and differences between the latices.

The main objective of the present study is to delineate the effect of the surfactants added to formulations as post-stabilizers. These will be referred to as "formulation surfactants". They are added during the mixing of pigments with latex and other components to produce the final coating formulation. Surfactants are employed in the synthesis of the latex, and are generally anionic or a combination of anionic and nonionic types. Anionic surfactants generally provide small median particle-size latices. Nonionic surfactants added during formulation of the coating provide additional stability to the dispersed components (i.e., titanium dioxide, calcium carbonate, silicates, etc.) present in a completed formulation. Nonionic surfactants provide better water-sensitivity and better color acceptance to the applied film than are observed if an anionic surfactant is used for the post-stabilization of dispersed components.

Kronberg and coworkers have investigated the adsorption of various surfactants on catalyst-fragment-stabilized polystyrene and polyvinyl chloride latices⁵. Increased adsorption on the surface of the latex is observed

when the hydrophilicity of nonionic nonylphenol surfactant decreased. It was also observed that nonionic surfactants, particularly as they become increasingly hydrophobic, are capable of displacing anionic surfactants from the surfaces of the two chemically different latices⁶.

The presence of formulation surfactants and hydrophobically-modified (e.g., with surfactant type structures), water-soluble polymers in formulations containing a variety of dispersed components of variable surface energies provide the possibility for a multitude of associations that could influence coating rheology. Formulations containing various nonionic and anionic formulation surfactants with different critical micellar concentrations will be examined in this paper. Coating film properties such as sag, gloss and scrub resistance will be discussed in addition to coatings rheology. The effect of associative thickeners on syneresis (phase separation) and pigment settling also is discussed.

Experimental

The materials and techniques used in this study are similar to those reported

previously¹⁻³. All of the formulations studied were prepared with the small-particle (117 nm), all-acrylic latex. The formulation surfactant was varied by selecting the following on the basis of differences in structure, CMC (critical micellar concentration)^{7,8} and HLB (hydrophilic-lipophilic balance) values. The surfactant concentration in the coating formulations was constant on a molar basis (4.28×10^{-3} mole/100g of formulation).

Nonionic surfactants: nonylphenols with averages of 40 and 4 units of ethylene oxide (Tergitol NP-40 and Tergitol NP-4, respectively, both from Union Carbide). The standard formulation surfactant used in previous studies¹⁻³ was a secondary alcohol having an average chain length of 13 carbon atoms with an average of 9 moles of ethylene oxide (Tergitol 15-S-9, from Union Carbide).

Anionic surfactants: a sodium dioctyl sulfosuccinate (Aerosol OT from American Cyanamid) and an alkylaryl polyether sulfonate (Triton X-200, from Rohm and Haas).

Structures, molecular weights, CMC and HLB values of these surfactants are given in Table 1. Data in Table 1

represent the average properties of polydispersed surfactant samples⁸.




Scrub resistances of dry films were determined using an Epprecht Instrument. The test procedure is very similar to the method described in ASTM standards⁹. Experimental error was between 22% (for the lowest values) and 2.3% (for the highest values). Coating films with scrub resistance values greater than 2000 were considered excellent and the tests were discontinued due to time limitations.

Various properties of the formulations are listed in Table 2 (57 PVC) and Table 3 (35 PVC). They include the thickener concentration (based on the total weight of the formulation), Stormer viscosity (in Krieb units, KU), shear viscosities at s^{-1} (LSV) and $104 s^{-1}$ (HSV) shear rates, sag ratings, scrub resistance and gloss at 750 degree angle. Table 2 does not contain gloss data as 57 PVC formulations result in flat coating films.

Studies on phase separation and pigment settling are limited to

Table 1

Properties of surfactants

Surfactant	Structure	MW	CMC ($\times 10^4$ M) (weight %)	HLB
Tergitol NP-40	C_9H_{19} -  -(OCH ₂ CH ₂) ₄₀ OH	1980	8.1 (.160)	17.8
Triton X-200	C_8H_{17} -  -(OCH ₂ CH ₂) ₂ SO ₃ Na	380	6.1 (.023)	12.1
Aerosol OT	$C_8H_{17}COOCH_2$ $C_8H_{17}COOCH-SO_3Na$	444	6.8 (.030)	14.3
Tergitol 15S9	$CH_3(CH_2)_5-CH-(CH_2)_5CH_3$ $(OCH_2CH_2)_9OH$	596	.52 (.003)	13.3
Tergitol NP-4	C_9H_{19} -  -(OCH ₂ CH ₂) ₄ OH	396	Insoluble	8.9

coating formulations containing Tergitol 15-S-9 (standard formulation surfactant used in previous studies). The height of the separated top layer was measured as a function of time, and recorded as a percentage of the total height of the sample (Table 4). After a one month period, the original paint containers were opened and checked for settling. In severe cases very hard crusts, difficult to redisperse, were formed at the bottom of the container. These were assigned a rating of 5. The cases where no pigment settling was observed were assigned a rating of 1.

Results and discussion

As mentioned in the introduction section, latices used in coatings contain surfactant(s) used in their synthesis. An anionic surfactant is generally employed to achieve a small particle-size latex, such as the 117 nm latex employed in this study. In general, anionic surfactants are used at 0.2 - 2.0% (based on monomer) in the synthesis¹⁰. Calculations reveal that the upper limit (2.0%) is about 25% of the concentration of formulation surfactants employed in these studies; however, the all-acrylic latex used in these studies also contain surface carboxylic acid groups¹¹. Such latices require extremely low levels of surfactants during the synthesis. Similar latices prepared by Sperry and co-workers¹² employ approximately 0.05% anionic surfactants. When the latex is

Table 2

Properties of 57 PVC coating formulations containing a small-particle, all-acrylic latex

Surfactant	Conc.* (Wt.%)	KU ^b	LSV ^c (Pa.s)	HSV ^d (mPa.s)	Sag ^e Rating	Scrab/Resistance
Thickener: HEUR 100						
NP-40	0.71	77	0.82	92	5	290
	0.90	88	1.29	143	5	180
	1.06	102	1.89	204	6	180
	1.35	118	3.26	310	7	90
NP-4	0.53	73	0.24	43	3	540
	0.77	89	0.92	75	6	500
	1.03	97	1.54	125	7	450
	1.52	120	3.87	253	9	320
OT	0.60	80	0.86	54	7	350
	0.80	89	1.14	90	7	290
	1.05	104	2.70	138	7	230
	1.31	120	3.50	209	8	150
X-200	0.62	82	1.03	70	5	430
	0.70	90	1.29	89	6	390
	0.84	104	1.99	126	7	330
	1.04	121	3.83	182	8	310
Thickener: HEUR 200						
NP-40	0.91	73	3.01	86	20	1100
	1.16	86	3.86	129	25	850
	1.50	102	6.37	190	35	760
	1.81	120	7.19	251	40	630
NP-4	0.56	89	1.41	79	6	>2000
	0.61	94	1.99	92	8	>2000
	0.74	104	3.07	122	9	>2000
	0.90	118	3.69	158	14	1800
OT	0.86	77	2.22	92	14	820
	1.02	89	3.21	119	16	710
	1.23	102	4.19	157	20	510
	1.56	121	6.27	221	25	350
X-200	0.94	75	3.93	79	20	1230
	1.13	86	4.98	109	30	930
	1.45	100	7.62	155	40	660
	1.71	114	8.91	207	50	450
Thickener: HEUR 708						
NP-40	0.50	76	0.64	85	5	1200
	0.61	90	0.96	134	5	920
	0.77	102	1.94	199	7	680
	0.96	116	3.06	284	8	450
NP-4	0.30	77	0.49	44	5	>2000
	0.40	86	1.29	60	6	1800
	0.57	100	2.36	105	7	1200
	0.68	116	3.65	160	9	850
OT	0.34	76	0.93	54	5	1600
	0.43	90	1.60	92	6	1250
	0.56	102	2.21	119	6	910
	0.66	116	3.56	169	8	650
X-200	0.42	78	0.98	68	5	1200
	0.50	91	1.38	96	6	750
	0.58	100	2.21	133	7	490
	0.73	112	3.44	182	8	330

Thickener: SMAT

NP-40	0.73	83	1.09	140	4	510
	0.85	95	1.83	187	4	270
	0.95	108	2.67	236	6	180
	1.15	123	4.61	325	6	140
NP-4	0.32	85	3.50	50	13	1200
	0.37	95	3.92	57	14	1050
	0.49	106	6.07	77	14	820
	0.67	120	8.85	105	16	680
OT	0.49	83	1.08	84	5	300
	0.57	94	1.86	108	6	220
	0.65	105	2.41	125	7	180
	0.84	122	4.89	192	8	160
X-200	0.52	81	0.68	73	4	400
	0.60	89	1.01	105	5	290
	0.71	104	1.86	140	6	240
	0.86	120	3.31	212	8	180

Thickener: HEC

NP-40	0.38	86	3.87	44	14	890
	0.47	105	6.82	52	16	730
	0.63	119	12.40	72	25	420
NP-4	0.32	80	4.08	44	14	1200
	0.43	199	7.62	49	16	710
	0.58	114	14.25	60	25	380
	OT	0.37	85	5.46	45	14
OT	0.44	103	6.83	49	16	350
	0.60	118	13.56	59	25	290
	X-200	0.35	84	3.70	39	14
X-200	0.44	103	6.41	46	16	450
	0.62	120	13.77	61	25	320

*Concentration based on total weight of coating formulation.

^bStormer viscosity in Krebs units.

^cViscosity at 2 s⁻¹ shear rate.

^dViscosity at 10,000 s⁻¹ shear rate.

^eDetermined by Leneta Anti-Sag test.

^fDetermined according to ASTM Standards, D2486-74a.

added to the coating formulation, the latter level is less than 1% of the concentration of the formulation surfactants. Thus, the influence of the synthesis surfactant would be insignificant compared to that of the formulation surfactant.

The data in Tables 2 and 3 are obtained from coating formulations containing two nonionic formulation surfactants (Tergitol NP-40 and NP-4) and two anionic surfactants (Aerosol OT and Triton X-200). These are analyzed with the data from Part I¹ which employed Tergitol 15-S-9. The data will be selectively presented in graphical form in order to emphasize important trends.

High shear viscosities

Tergitol NP-4 is more hydrophobic than NP-40 (Table 1); it is dispersible, not water-soluble. A difference in hydrophobic interactions between these two nonionic surfactants would be expected. The effect of surfactant on the variation of HSV with thickener concentration is illustrated in Figures 1 and 2 for NP-40 and NP-4 formulations, respectively. The more interesting observation is the nature of this effect on each H-M, W-SP. The HSV performance of HEUR 708, 100 and SMAT formulations decreases in magnitude, whereas that of HEUR 200 is slightly improved as the formulation surfactant becomes more hydrophobic. HEC does not exhibit a significant change.

In order to facilitate a comparative analysis among surfactant effects, the slopes of the lines corresponding to each thickener in Figures 1 and 2 and similar figures for other surfactant formulations are used. Since the slope does not provide an indication of the actual concentration of thickener present in a formulation, another parameter, the concentration (wt.%) of a thickener required to produce a HSV of 100 mPa.s, also is used in the analysis. Analysis of HSV and LSV data in terms of the slopes (^sHSV, Figure 3) and the concentration (Wt.%) required to achieve 100 mPa.s (^wHSV, Figure 4) exhibit interesting trends with respect to each thickener. The anionic and nonionic surfactants are segregated in Figures 3 and 4 according to their CMC values.

Table 3
Properties of 35 PVC coating formulations containing a small-particle, all-acrylic latex

Surfactant	Conc. ^a (Wt.%)	KU ^a	LSV ^a (Pa.s)	HSV ^a (mPa.s)	Sag ^a Rating	Scrub ^b Resistance	Gloss ^b (at75°)
Thickener: HEUR 100							
NP-40	0.52	72	0.49	80	4	>2000	33
	0.62	82	0.76	89	5	>2000	28
	0.71	89	1.08	120	6	1800	30
	1.01	104	1.78	224	7	1200	35
NP-4	0.25	76	0.74	40	7	>2000	14
	0.39	88	1.70	46	9	>2000	16
	0.60	100	1.79	71	13	>2000	19
	0.77	112	1.97	118	14	>2000	22
OT	0.41	72	0.81	40	6	>2000	26
	0.51	89	1.04	58	8	>2000	27
	0.73	95	1.54	73	9	>2000	29
	1.02	110	2.72	162	13	1800	36
X-200	0.51	77	0.61	59	6	>2000	39
	0.58	88	0.91	75	7	1800	36
	0.75	100	1.32	120	8	1400	37
	0.92	115	2.90	179	9	1100	39
Thickener: HEUR 200							
NP-40	0.62	72	2.04	37	18	>2000	34
	1.05	95	4.92	82	40	>2000	34
	1.56	99	7.13	128	45	>2000	36
	1.74	116	11.92	192	>60	1800	36
NP-4	0.66	82	1.28	70	13	>2000	41
	0.74	89	1.56	82	13	>2000	41
	0.88	101	2.58	109	14	>2000	39
	1.08	120	4.47	153	18	>2000	38
OT	0.93	77	4.30	70	30	>2000	40
	1.06	87	5.44	88	35	>2000	40
	1.35	101	7.80	128	50	>2000	40
	1.57	116	9.95	167	>60	>2000	37
X-200	0.77	76	4.37	46	20	>2000	40
	0.96	90	5.16	58	30	>2000	43
	1.25	96	7.39	90	45	1550	41
	1.72	113	12.35	160	>60	1000	37
Thickener: HEUR 708							
NP-40	0.38	72	0.37	46	6	>2000	31
	0.57	88	0.53	81	6	1100	33
	0.91	114	1.60	199	8	960	36
	1.06	123	1.76	258	9	670	38
NP-4	0.22	80	0.61	32	6	>2000	19
	0.30	91	0.81	48	7	>2000	20
	0.45	104	1.48	75	8	>2000	29
	0.65	120	2.11	123	9	>2000	36
OT	0.39	83	0.68	48	7	>2000	33
	0.50	94	0.93	69	8	>2000	31
	0.65	108	1.40	113	8	>2000	32
	0.74	119	1.84	145	9	1600	36
X-200	0.43	83	0.51	49	6	>2000	43
	0.51	92	0.77	69	7	>2000	39
	0.61	102	1.11	89	8	>2000	41
	0.77	118	1.73	155	10	1330	40
Thickener: SMAT							
NP-40	0.68	77	0.66	135	6	>2000	66
	0.80	89	1.11	177	7	1800	67
	0.88	100	1.33	209	7	1200	51
	1.08	113	2.80	298	8	820	76
NP-4	0.38	77	1.33	70	6	>2000	41
	0.40	90	2.13	81	8	>2000	34
	0.49	104	3.69	109	10	>2000	44
	0.62	118	4.85	135	16	>2000	44
OT	0.53	79	0.71	99	6	>2000	52
	0.66	89	1.28	135	6	1200	56
	0.76	100	1.74	167	7	820	70
	0.87	112	2.95	214	9	560	75
X-200	0.56	72	0.52	92	5	800	72
	0.60	82	0.75	105	6	510	50
	0.73	100	1.56	165	7	450	72
	0.94	112	2.43	236	8	380	62

a For definitions of the terms see footnote to Table 1.

b Determined by Gardner Multi-Angle Glossmeter.

The anionic surfactants included in these figures were selected on the basis of their structures. Octylphenol with an ethylene oxide chain and pendant sulfonate ester (Triton X-200) has a CMC value of 0.023 wt. % (6.1×10^{-4} M); sodium dioctylsulfosuccinate (Aerosol OT), a branched structure (Table 1), has a CMC value of 0.03 wt. % (6.8×10^{-4} M). The trends observed in Figures 3 and 4 with respect to each H-M, W-SP are not related to the ionic or nonionic nature of the surfactant, but to their CMC values. HSVs of HEC are not affected by the formulation surfactants.

The efficiency at high shear rates decreases with decreasing CMC of the surfactant when the thickener is HEUR 708, HEUR 100 or styrene/maleic acid teropolymer, SMAT. The greatest HSV sensitivity to formulation surfactant variation is observed in coating formulations containing the ionic thickener, SMAT (Figure 3). The lowest high-shear-viscosities are observed in formulations containing the low ethoxylate nonylphenol surfactant, NP-4, except in formulations containing HEUR 200, where a slight increase in HSV is evident. The 57 and 35 PVC data follow a pattern observed in all previous studies and confirm that the thickening mechanism of HEUR 200 is opposite to that of other associative thickeners. The low-shear viscosity data, discussed in the following section also are consistent with this trend.

Low shear viscosities and sag resistance

The low-shear viscosity (LSV, viscosity at 2 s^{-1} shear rate) dependence on the thickener concentration is illustrated in Figures 5-7 for 57 PVC formulations containing NP-40, NP-4 and Aerosol OT as formulation surfactants. Slopes of the lines of LSV versus thickener concentration (wt. %) for each thickener ($^{\text{S}}\text{LSV}$) are illustrated in Figure 8.

The LSV performance of HEC does not depend on the formulation surfactant. This is consistent with the sag data which also are constant (Table 2). Associative thickener formulations are sensitive to surfactant variations; however, a pronounced sensitivity is exhibited only by SMAT, consistent with the sag data of coating formulations containing that thickener. Sag ratings and LSVs dependence on thickener concentration for formulations containing various surfactants and SMAT are illustrated in Figure 9. The greatest sag resistance and highest LSVs are observed with the most hydrophobic surfactant. This is a difference between SMAT and the two H-M, W-SPs, HEUR 708 and HEUR 100, which usually impart responses similar to SMAT. SMAT is the only ionic thickener in this series; it has a distinctly different chemical structure from the HEUR-type thickeners¹.

The lower gloss (Table 2) of NP-4/SMAT formulations support the pigment flocculation mechanism. Neither the LSVs nor the sag values are large enough to detect a sensitivity to surfactant variation in HEUR 708 and HEUR 100 thickened formulations. The lowest sag values with NP-4 in both 57 and 35 PVC formulations are observed in HEUR 200 thickened coatings (Figures 10 and 11). In prior studies with the small particle size latex, it has been observed that HEUR 200 tends to associate with itself in the continuous medium¹. If the hydrophobic NP-4 surfactant disrupts these associations via cohesive interactions, it results in lower LSVs. Hydrophobic interactions between macromolecules and surfactants are well documented¹³. The variation of sag values with formulation surfactant (Table 2 and Figures 10 and 11) illustrates the limitation of LSVs as an indicator of sag performance. The LSV data obtained at 2 s^{-1} do not parallel sag variations when the formulation surfactant is changed (Figures 10 and 11). The lowest HEUR 200 formulation sag

Table 4

Phase Separation and Pigment Settling behaviour of coating formulations containing 117nm(Dia.) All acrylic latex (PVC = 57; %NVV = 32)

W-S Polymer	MW ($\times 10^{-4}$) ^a	Conc.(Wt.%)	KU	LSV(Pa.s) ^b	%Phase Sep. ^c	Pigment Sett. ^d
HEUR 100	1.1	0.52	86	1.05	35	1
HEUR 200	9.4	0.84	93	2.80	0	1
HEUR L75	2.8	0.99	90	1.33	16	1
HEUR 8500	1.1	0.51	91	1.62	16	2
SMAT	3.2	0.62	87	1.48	4.5	5
HEUR 708	3.7	0.40	93	1.48	19	1
HEC	6.8	1.76	84	4.77	23	1
HEC	100	0.34	85	4.82	0	1

^aWeight average molecular weights of associative thickeners (from Ref. 1) and viscosity average molecular weights of HECs (from Ref. 12).^bLow-Shear viscosity (i.e., viscosity at 2 s^{-1} shear rate).^cHeight of the separated top layer as a percentage of the total height of the sample.^dPigment settling- 1 indicate no settling and 5 indicate severe settling.

ratings are observed with the lowest CMC surfactant, but this combination does not result in dissimilar viscosities. The lack of a correlation is also evident in comparing the LSV and sag data between HEC and HEUR 200 (Table 2) coatings. This poor correlation is the result of several factors. Experimentally, the LSV determination does not have the precision of HSV measurements. In addition, the sagging process occurs at very low shear rates (ca. $<1 \text{ s}^{-1}$)⁽¹⁰⁾. Under these conditions, not only the shear viscosity, but also elastic parameters such as G' (storage modulus) are important⁽¹⁰⁾. Systems which do not exhibit differences at 2 s^{-1} shear rate (the reference value used in these studies due to experimental limitations) could be significantly different at very low shear-rates highlighting the value of sag data. The very high sag values in HEUR 200 coatings with the high CMC surfactants indicate the presence of a large amount of weak, inter-species interactions. These could include flocculation of dispersed particles and intermolecular interactions among HEUR 200 molecules. The more hydrophobic, low CMC surfactant appears capable of disrupting these interactions in the HEUR 200 thickened formulations.

Gloss

The gloss of the coating films is significantly lowered by NP-4 when the thickener is HEUR 708, HEUR 100 or SMAT (Table III), but the gloss of HEUR 200 thickened formulations is not dependent on the formulation surfactant. This observation (i.e., the different behaviour between HEUR 200 and other associative thickeners) is consistent with the trends in rheological performance. SMAT provides coating films with the highest gloss. The low gloss values observed with the NP-4 and SMAT combination are equivalent to the highest gloss observed with other thickeners.

Although the gloss of HEUR 708 formulations are comparable to those containing HEUR 100 or 200, HEUR 708 is observed to yield films with considerably lower gloss than formulations containing TiO_2 as the only pigment. These data will be discussed in a future article.

Phase separation and pigment settling

Phase separation involves the settlement of dispersed components under gravity. The shear rates pertinent to this process⁽¹⁴⁾ are much lower (i.e., $<1 \text{ s}^{-1}$) than the accessible shear rates of the instruments used in these studies. The data in Table 4 pertain to approximately 90 KU formulations containing the small-particle, all-acrylic latex at 57 PVC and 32 %NVV. Although these formulations have approximately the same Stormer viscosity, their low-shear viscosities (LSV, viscosity at 2 s^{-1} shear rate) differ significantly (Table 4). A weak relationship between the LSV and the extent of phase separation is evident. The lower the LSV, the higher the extent of separation. A major deviation is exhibited by the formulation thickened with a low molecular weight HEC. Both the molecular weight and LSV of this formulation are higher than those of the associative thickeners, except HEUR 200 (Table 4), formulations. The lower phase separation in associative thickener formulations suggests an influence on hydrophobic-modification on phase separation. Additional studies are warranted in this area.

SMAT is the only thickener which caused pigment settling in these formulations; it is the only ionic thickener in the series. Coating formulations containing only TiO_2 as the pigment did not exhibit pigment settling when thickened with SMAT, indicating that it is the flocculation of the large extender pigments that is occurring.

Scrub resistance

Although scrub resistance data do not provide insights into the thickening mechanism, they are useful in determining the effect of thickeners and surfactants on dry film properties. The scrub resistance of 35 PVC coatings is superior to that of 57 PVC coatings (Tables 2 and 3), which is not surprising; more binder is available to yield better film integrity in 35 PVC formulations. Most of the 35 PVC coatings were able to withstand 2000 scrub cycles without failure.

Differences among thickener/surfactant pairs are observed in the 57 PVC coatings. As the concentration of thickener is increased, the scrub resistance is decreased in all systems. A similar trend is evident as the hydrophilicity of the surfactant increases. The best scrub resistance is observed with the most hydrophobic surfactant, NP-4. Anionic surfactant/SMAT (i.e., the ionic thickener) combinations result in poor scrub resistance. These trends are illustrated in Figures 12 and 13 for NP-4 and X-200 formulation surfactants, and can be attributed to the water sensitivity imparted to coatings by the thickeners and surfactants. It should be noted that, at 35 PVC less than 2000 scrub values are observed (Table 3) only under conditions where the thickener and surfactants are very hydrophilic.

The differences in scrub data among thickeners cannot be explained by water-sensitivity alone. The surprising result is the extremely low scrub resistance exhibited by HEUR 100 (Figures 15 and 16, Table 2). This is the most hydrophobic (i.e., the lowest aqueous solution surface tension is observed, Table 2 of reference 1) and lowest molecular weight (10,000) associative thickener studied. Thus, the lower scrub resistance cannot be due to water-sensitivity alone. HEUR 100 may be able to plastisize the binder which in the abrasive scrub medium would facilitate greater film disintegration. The ratio between the HEUR 100 and latex polymer is significantly lower in 35 PVC films and improved scrub resistance is observed.

Conclusions

The rheological behaviour of hydrophobically-modified, water-soluble polymers in latex coating formulations is affected by the formulation surfactants. The effects observed with respect to each thickener are related to the critical micellar concentration of the surfactants.

Figure 1

High-Shear-Viscosity (HSV) Dependence on Weight Percent (Wt.%) Thickener Required to Attain Stormer Viscosities of 80, 90, 105 and 120 KUs in 57 PVC, 32 %NVV Formulations Containing Small Particle (117 nm), All-Acrylic Latex and Tergitol NP-40 as Formulation Surfactant. □, HEC; ○, SMAT; ◊, HEUR 708; ◇, HEUR 200; HEUR 100.

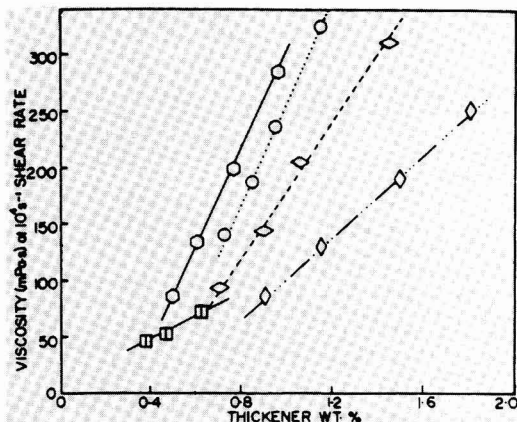
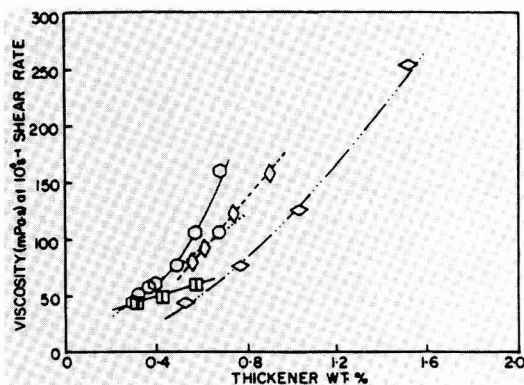


Figure 2

HSV Dependence on Wt.% Thickener Required to Attain Stormer Viscosities of 80, 90, 105 and 120 KUs in 57 PVC, 32 %NVV Formulations containing Small Particle (117 nm), All-Acrylic Latex and Tergitol NP-4 as Formulation Surfactant. Thickener symbols are given in Figure 1.



Results of the study are consistent with trends observed in other investigations (e.g. HEUR 200 thickens by a mechanism distinctly different from the other associative thickeners); however, the role of the MC of the surfactant in the matrix of different thickener architectures¹⁵ has not been defined. A large multiple of the formulation surfactant's MC, approximately that

used in a coating, is required to maximize solution viscosities¹⁶ and this concentration is dependent on the thickener's molecular weight, architecture and hydrophobe placement frequency.

Syneresis appears to be related to the molecular weight and the presence of hydrophobes in the thickener structure; a clear understanding of the

phenomenon requires additional study. Pigment settling does not appear to be a problem with the nonionic associative thickeners. The gloss data are complex and will be addressed in future investigations.

Acknowledgement

The financial support for this study by Hercules Inc, is gratefully acknowledged.

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Figure 3

Dependence of HSV Efficiency (in Terms of slopes (mPa s/Thickener Wt.%) of Thickeners in 57 PVC, 32 %NVV Formulations Containing Small Particle (117 nm), All-Acrylic Latex, on Formulation Surfactant. Thickener symbols are given in Figure 1.

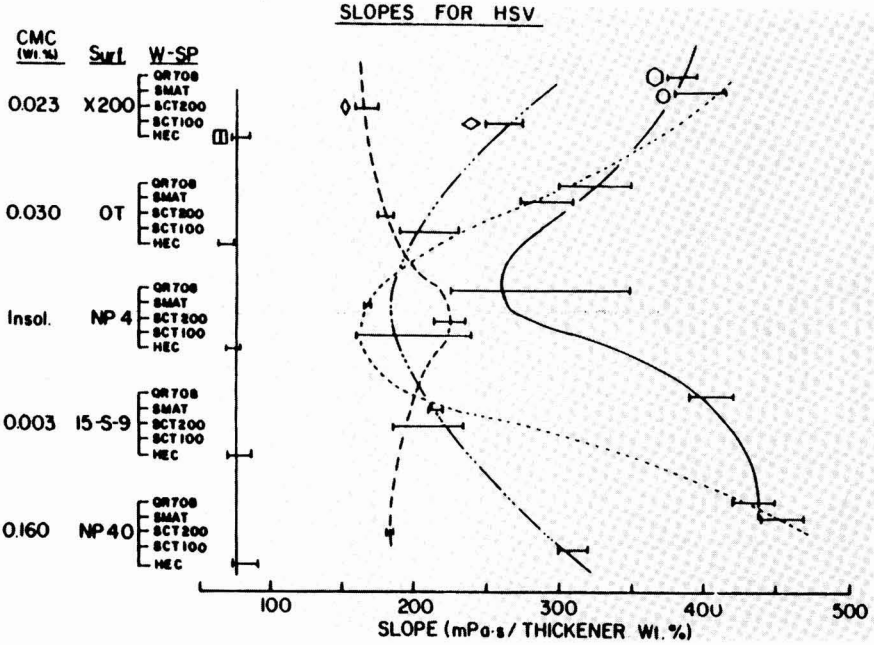


Figure 4

Dependence of Wt.% required to Attain 100 mPa s at 10^4 s^{-1} Shear Rate, on Formulation Surfactant in 57 PVC, 32 %NVV Formulations containing Small Particle (117 nm), all-Acrylic Latex. Thickener symbols are given in Figure 1.

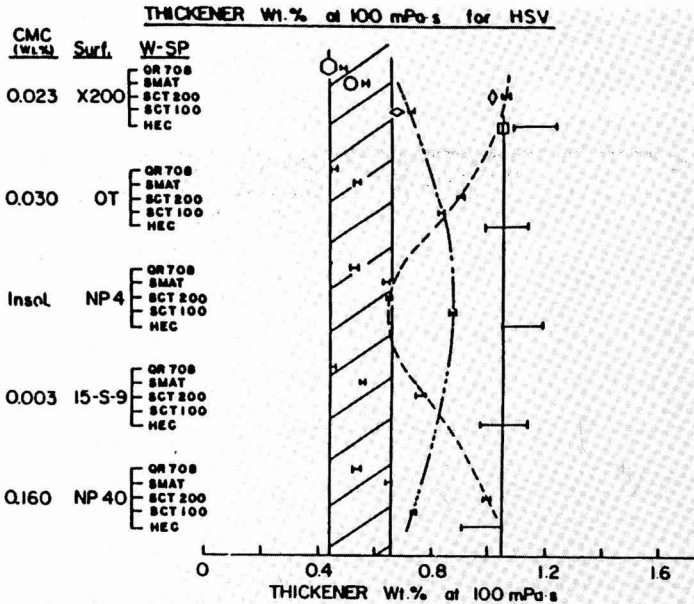


Figure 5

Low Shear Viscosity (LSV) Dependence on Wt.% Thickener Required to Attain Stormer Viscosities of 80, 90, 105 and 120 KUs in 57 PVC, 32 %NVV Formulations Containing small Particle (117 nm), All-Acrylic Latex and Tergitol NP-40 as formulation Surfactant. Thickener symbols are given in Figure 1.

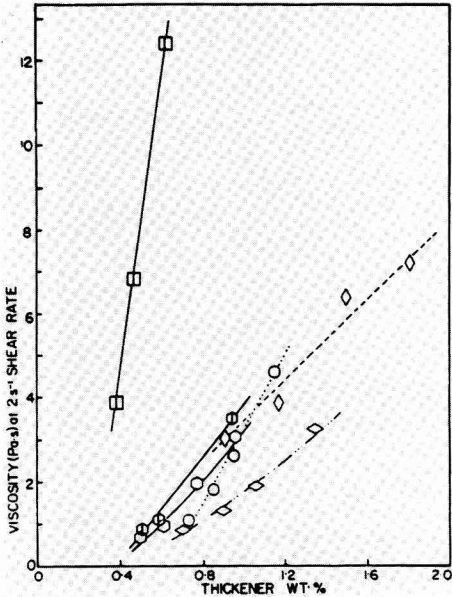


Figure 6

LSV Dependence on Wt.% Thickener Required to attain Stormer Viscosities of 80, 90, 105 and 120 KUs in 57 PVC, 32 %NVV Formulations containing small Particle (117 nm), all-Acrylic Latex and Tergitol NP-4 as Formulation Surfactant. Thickener symbols are given in Figure 1.

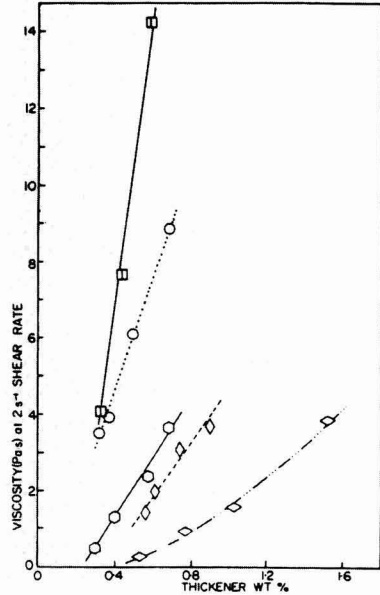


Figure 7

Low Shear Viscosity (LSV) Dependence on Wt.% Thickener Required to Attain Stormer Viscosities of 80, 90, 105 and 120 KUs in 57 PVC, 32 %NVV Formulations containing Small Particle (117 nm), all-Acrylic Latex and Aerosol OT as Formulation Surfactant. Thickener symbols are given in Figure 1.

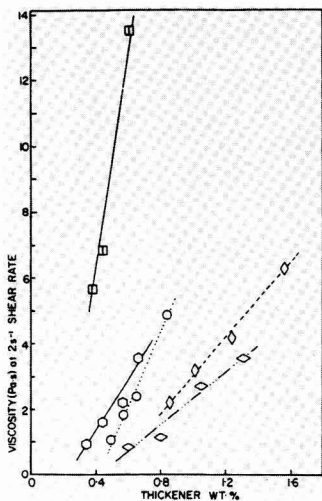


Figure 8

Dependence of LSV Efficiency (in Terms of Slopes (Pa.s/Thickener Wt.%) of Thickeners in 57 PVC, 32 %NVV Formulations Containing Small Particle (117 nm), All-Acrylic Latex, on formulation Surfactant. Thickener symbols are given in Figure 1.

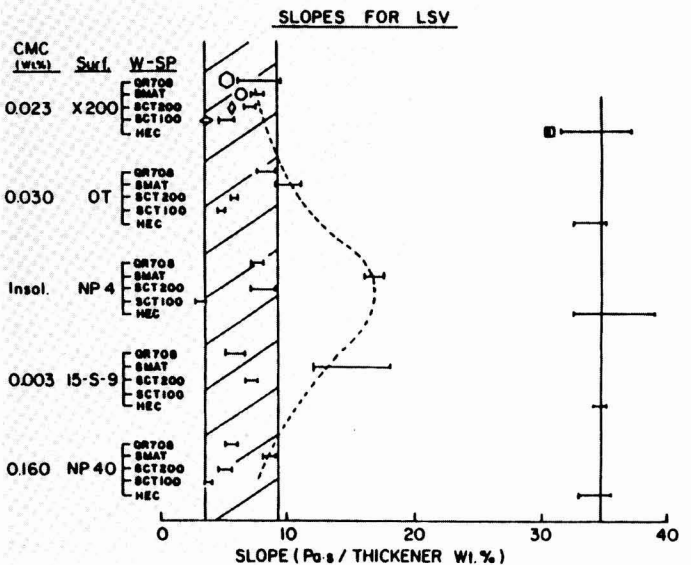


Figure 9

Sag Rating and LSV Dependence on Thickener Wt.% in 57 PVC, 32 %NVV Formulations Thickened with SMAT. Formulation Surfactant is Varied: □ ,NP-40; ▽ ,NP-4; ◇ ,15-S-9; △ ,OT; ○ ,X-200. (Open symbols - Sag Rating, Closed symbols - LSV).

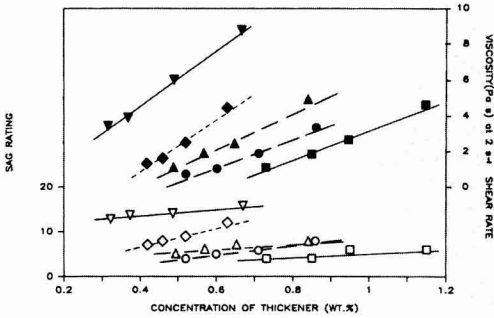


Figure 10

Sag Rating and LSV Dependence on Thickener Wt.% in 57 PVC, 32 %NVV Formulations Thickened with HEUR 200. Formulation Surfactant is Varied. Surfactant symbols are given in Figure 9.

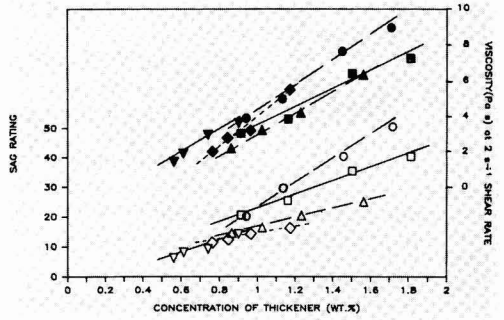


Figure 11

Sag Rating and LSV Dependence on thickener Wt.% in 35 PVC, 32 %NVV Formulations Thickened with HEUR 200. Formulation surfactant is Varied. Surfactant symbols are given in Figure 9.

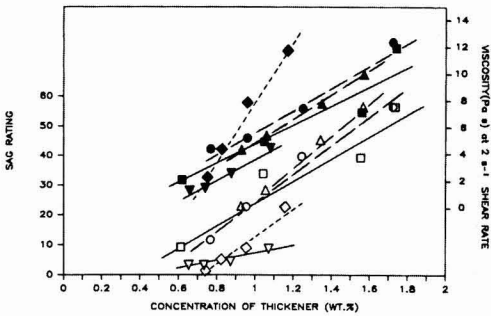


Figure 12

Dependence of Scrub Resistance on Thickener Wt.% in 57 PVC, 32 %NVV Formulations Containing Tergitol NP-4 Formulation Surfactant. Thickener symbols are given in Figure 1.

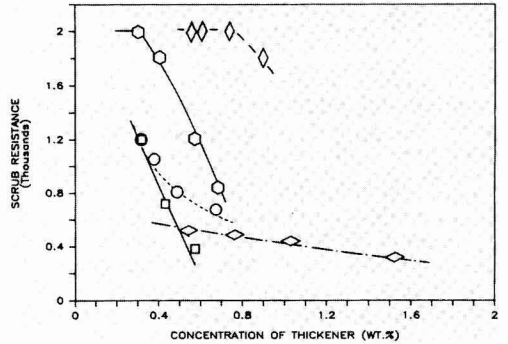
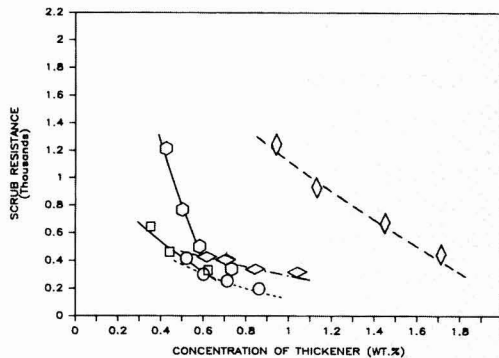


Figure 13

Dependence of Scrub Resistance on Thickener Wt.% in 57 PVC, 32 %NVV Formulations Containing Triton X-200 Formulation Surfactant. Thickener symbols are given in Figure 1.



Paint and Surface Coatings

Theory and Practice



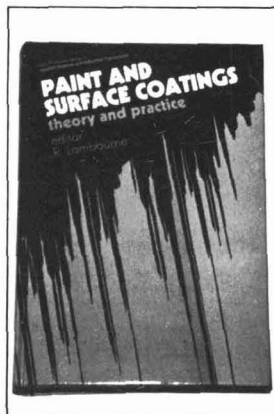
Edited by R. LAMBOURNE,
Technical Manager,
INDCOLLAG (Industrial Colloid
Advisory Group), Department of
Physical Chemistry, University of
Bristol.

696 pages; Published April 1987; £81.00 (incl. of p+p,
overseas orders are sent surface mail).

CONTRIBUTORS:

- D. A. Ansdell, Technical Manager, Automotive Products*.
- J. Bentley, Senior Scientist, Research Department*.
- T. R. Bullett, Retired. Formerly Research Director, Paint Research Association,
Teddington, Middx.
- A. Doroszkowski, Research Department*.
- F. K. Farkas, Consultant, FKF & Associates.
- J. A. Graystone, Technical Manager, Research Department*.
- R. A. Jeffs, Retired. Formerly with Research Department*.
- W. Jones, Research Department*.
- R. Lambourne, University of Bristol.
- A. H. Mawby, Director, Refinish Marketing, PPG Industries (UK) Ltd,
Ladywood, Birmingham.
- Miss J. F. Rolinson, European Technical Manager for Products and Materials*.
- T. A. Strivens, Senior Scientist, Research Department*.
- G. P. A. Turner, Technical Manager, Industrial Coatings Research*.

* ICI Paints Division, Slough.



CONTENTS: Paint Composition and Applications—A General Introduction; Organic Film Formers; Pigments for Paints; Solvents, Thinners and Diluents; Additives for Paint; The Physical Chemistry of Dispersions; Particle Size and Size Measurement; The Industrial Paint Making Process; Coatings for Buildings; Automotive Paints; Automotive Refinish Paints; General Industrial Paints; An Introduction to Rheology; The Rheology of Paints; Mechanical Properties of Paints and Coatings; Appearance Qualities of Paint—Basic Concepts; Specification and Control of Appearance; Durability Testing.

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Glycol ether use in polyurethane coatings

by R. A. Heckman, ARCO Chemical Company, Newtown Square, Pennsylvania, USA.

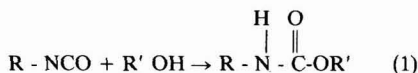
This paper addresses the use of glycol ether solvents in two-component air-drying polyurethane coatings. Such use has been avoided in the past due to the reactivity of the hydroxyl group of glycol ethers with isocyanate resins. The propylene-based glycol ethers, however, have predominantly secondary hydroxyl groups, typically greater than 98% and are significantly less reactive towards isocyanate resins. Ultimate coating performance depends on the relative rates of reaction of glycol ether solvents and polyol resins with isocyanate resins. Data presented here show that propylene glycol methyl ether (PM) may be successfully used as a solvent in these coatings with minimal degradation of film performance. A significant advantage of PM use is enhanced solvent release from urethane coatings relative to the conventional glycol ether ester solvents.

The advent of two-component polyurethane coatings represented a significant advance in coatings technology, with substantial improvements in durability and chemical and water resistance at minimal cost to the user. The variety of isocyanates and polyols available gave coatings formulators considerable flexibility in development of new cost effective formulations. Thus, the two-component polyurethane coatings have taken a substantial share of the current coatings market.

Along with the development of two-component polyurethane coatings, however, came a requirement for additional high-performance solvents to dissolve the isocyanate and polyol resins and to carry them intact into the final formulation mixtures. Specifically, strong active solvents are required which show no reactivity with the isocyanate mechanism of polyurethane formation. Esters and ketones adequately fit the requirements. Solvents which have come to be the most commonly used include n-butyl acetate, methyl ethyl ketone (MEK) and,

most particularly, ethylene glycol ethyl ether acetate (EEA). Some hydrocarbons such as xylene are also frequently used in diluents.

Glycol ethers and alcohols, although used with most other coatings resin types, have historically been inappropriate for two-component polyurethane coatings due to the reactivity of the isocyanate resins with the free hydroxyl group will initially react with an isocyanate group to form a urethane as in Equation 1.



The reaction is detrimental to film formation in that the reaction of an isocyanate with a monofunctional alcohol is essentially a chain termination step, interrupting the formation of the very high molecular weight polymers which contribute to the outstanding chemical resistance and physical durability of polyurethane coatings. Thus, film formation under such circumstances will be adversely affected, resulting in inferior chemical resistance, for example. The relative reactivities of primary and secondary alcohols with isocyanates is well-known, with primary alcohols being several times more reactive.

The purpose of this paper is to explore the use of propylene glycol methyl ether (PM) and propylene glycol t-butyl ether (PTB) as solvents for two-component polyurethane coatings. These solvents have only relatively recently been available cheaply and in large quantity and their use has not been thoroughly explored earlier. Both solvents are predominantly secondary hydroxyl glycol ethers and thus are expected to show substantially diminished reactivity toward isocyanates relative to ethylene glycol ethyl ether (EE). The effect of PM and PTB on film formation properties will be discussed.

Solvents chosen for this study are shown in Table 1, along with some of the pertinent physical properties of those solvents. The structures of the

solvents are given in Figure 1. Of the solvents shown, ethylene glycol ethyl ether acetate (EEA) is recognised as the conventional glycol ether ester solvent for two-component polyurethane coatings, while propylene glycol methyl ether acetate (PMA) and ethyl 3-ethoxypropionate (EEP) are newer solvents with growing industry consumption. The historical volume growth of EEA can in large part be traced to the development of polyurethane coatings.

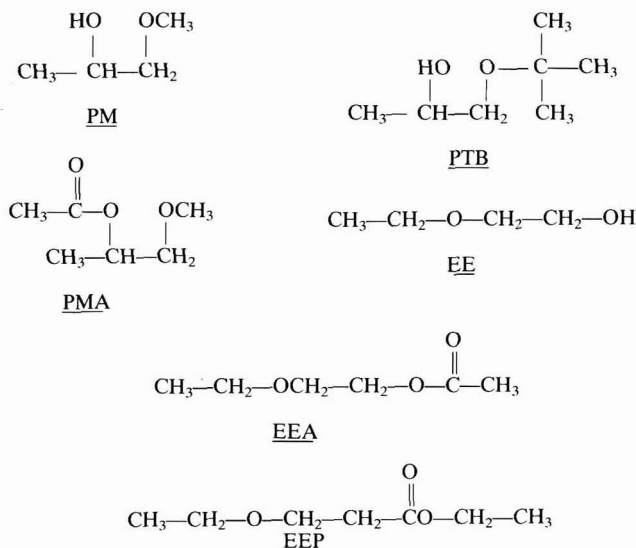
The structure of EE obviously precludes its use due to the presence of the hydroxyl group and,

Table 1
Solvents used in this study

Solvent	Evaporation Rate		Hansen Solubility Parameters		
	n-BuAc=1	DEE=1	δ_p	δ_h	δ_d
PM	0.66	18	3.3	7.7	7.5
PTB	0.25	47	2.1	6.2	7.3
PMA	0.34	35	2.4	4.2	7.5
EE	0.32	37	4.7	7.2	7.9
EEA	0.20	59	3.1	5.3	8.5
EEP	0.12	98	4.5	4.6	7.9
n-Butyl Acetate	1.00	12	3.1	3.2	8.3

Figure 1

Molecular structures of solvents used in this study



particularly, due to the fact that the hydroxyl group is on a primary carbon atom and is thus quite reactive toward isocyanates. In contrast, the newer glycol ether solvents PM and PTB can be produced with either primary or secondary OH groups. However, the current production techniques yield almost exclusively secondary hydroxyl glycol ethers. In fact, most PM producers supply material as greater than 98% primary hydroxyl solvent. As a result PM and, especially, PTB may be expected to be significantly less reactive than EE toward isocyanate functional groups.

Experimental

All materials used in this study were commercially available and were used without further purification. Two commercial aliphatic isocyanate resins were obtained as 100% N.V. for this study. Also used were four commercial polyols at various concentrations. Pertinent properties are given in Table 2.

The reactions of glycol ethers and polyols with isocyanate resins were followed titrimetrically as the

consumption of isocyanate. Samples of the reaction mixtures were withdrawn at intervals and reacted with an excess of dibutylamine. The excess

dibutylamine was then titrated with 0.5N HCL to the green-yellow endpoint of bromophenol blue. The concentration of unreacted isocyanate in the reaction mixture was then calculated.

Coatings were prepared as clear coat formulation and applied by spray to cold rolled steel test panels at a dry film thickness of 1.5-2.0 mils. For determination of retained solvent in dry films drawdowns were made on sealed paper test panels at a dry film thickness of 1.5 mils. Residual solvent levels in cured films were determined by extraction of the cured films.

Results and Discussion

The rate of reaction of aliphatic isocyanate A with PM and EE was determined as described above. Specifically, the resin was dissolved in the glycol ether at 50% N.V. at ambient temperature with 0.01% added catalyst (dibutyltin dilaurate). Samples were taken at intervals and the unreacted isocyanate levels were determined by titration. As expected the rate of reaction of EE was greater than

Table 2
Properties of resins used in this study

Aliphatic Isocyanates (100% N.V.)	Viscosity (20 C mPa-s)	Equivalent Weight Average % NCO	
A	12.000	191	22.0
B	2.700	181	23.3

Polyol	Type	% N.V. (Solvent)	Equivalent Weight Average	% OH
A	Polyester	65 (PMA/Xylene)	327	5.2
B	Polyester	80 (n-BuAc)	486	3.5
C	Polyester	75 (PMA)	266	6.4
D	Acrylic	60 (PMA)	1000	1.7

Table 3
Reaction * of glycol ethers with isocyanate resin A

Time, Hrs	% NCO	
	PM	EE
0	11.0	11.0
1	9.9	8.7
2	9.8	8.1
3	9.5	7.4
24	6.0	0.4

* 50% N.V. in PM or EE and 0.01% Catalyst T-12 [Dibutyl Tin Dilaurate]

that of PM by a factor of approximately 3 (Table 3). After 24 hours the isocyanate in the EE solution was essentially depleted whereas the isocyanate in the PM solution was still 50% active. The order of the reaction was not determined but is presumed on the basis of numerous literature studies to be first order in both hydroxyl and isocyanate in the simplest form of the rate law (Equation 2).

$$\frac{d[\text{NCO}]}{dt} = k [\text{NCO}] \cdot [\text{OH}] \quad (2)$$

A series of clear coatings formulations was prepared using various combinations of the polyol and isocyanate resins listed above. Various solvent combinations of glycol ether and glycol ether acetate were also used.

A polyester urethane coating formulation is shown in Table 4. The formulation uses two polyester polyols of different hydroxyl equivalent weight to modify some of the performance properties, such as flexibility, relative to either polyester alone. Five different solvents including PM and EE were evaluated in this formulation, *n*-butyl acetate, methyl ethyl ketone and xylene were present in all cases. Isocyanate A (as 100% N.V.) was mixed with the single solvents of interest immediately prior to formulating. After mixing the formulation was aged and test panels were prepared and air dried. All formulations gradually increased in viscosity, with gelation occurring in the PM and PMA formulations at 5-5.5 hours. The EE formulation, by contrast, never gelled. After an eight day air cure period the test panels were tested for hardness via a Sward rocker. The difference in hardness between the PM deposited film and any of the ester-deposited films is insignificant by this method. The EE-deposited film, however, became substantially softer with longer pot time, eventually failing to form a hard film at all. Thus, in this formulation the reaction of PM with isocyanate is sufficiently slow that competition with the polyol/isocyanate reaction does not significantly interfere with the film formation process.

Table 4

Clear two-component polyester urethane coating

Part A	Lbs
Polyester Resin B	37.6
Polyester Resin A	25.0
CAB 551.01 Cellulosic Resin (10% in PMA)	4.0
Dibutyltin Dilaurate Catalyst (1% in MEK)	0.4
Solvent (4/1/4/1 Glycol Ether or Ester/BuAc/MEK/Xylene)	55.0
Part B	
Isocyanate Resin A	33.8
Glycol Ether or Ester	10.6

Sward Hardness (8 Day Cure)

Pot Time Hrs	PMA	PM	EE	EEA	EEP
0	26	30	24	32	36
1	32	28	14	30	34
2	28	22	8	30	28
4	28	20	4	28	26
6	—	—	Tacky	24	22

Table 5

Clear air-dry two-component acrylic urethane coating

Component I	Lbs		
Acrylic Polyol D (60% N.V. in PMA)	493.6		
Solvent (EEA or PMA or PM)	277.3		
Dibutyltin Dilaurate Catalyst (1% in MEK)	4.3		
Surfactant SF - 1023 (1% in PMA)	21.4		
Component II			
Isocyanate Resin A (100% N.V.)	93.6		
EEA or PMA	109.8		
	PMA	PM	EEA
Viscosity (#4 Ford)			
Initial	29	26	25
1 Hr	33	28	32
3 Hr	37	31	37
5 Hr	45	34	42
Impact Resistance (In-Lbs)			
0 Hr	6	12	2
1 Hr	20	12	2
3 Hr	20	14	6
5 Hr	20	30	6
Cure (MEK Rubs)			
0 Hr	38	35	34
1 Hr	42	35	26
3 Hr	35	30	33
5 Hr	40	28	25
Water Resistance (Blistering ASTM D-714, 1 Week)			
0 Hr	10	10	10
1 Hr	9D	10	10/9F
3 Hr	9MD	10	9F
5 Hr	8F/9MD	9D	9F

Table 5 shows a clear coat formulation based on an acrylic polyol, again using isocyanate resin A. In this case the glycol ether PM was compared with PMA and EEA, the conventional urethane coatings solvents. As seen earlier the formulations gradually increased in viscosity to gellation in all systems at 6-8 hours. Test panels were evaluated for flexibility (as impact resistance) and resistance to methyl ethyl ketone and water. The EEA-based formulation gave the lowest impact resistance, consistent with good crosslinking and solvent release. Films formed from the PM-based formulation were slightly more flexible up to a pot life of 5 hours when the flexibility became substantially greater. Similarly, in the MEK resistance and water resistance tests the PM-based formulation was equivalent or slightly superior to either glycol ether acetate formulation at pot lives less than 5 hours.

A third clear coat formulation is shown in Table 6. Again, the performance properties of the films were not significantly different in either hardness or flexibility. The consumption of isocyanate was again monitored by titration. Even

after gellation of the formulations considerable unreacted isocyanate remained which was not consumed for several days. However, the residual isocyanate contents of the formulations at any point in time were strikingly similar for PM and PMA.

Table 6 also shows data for the content of non-evaporated solvent in each cured test film determined after 8 days dry time. The data demonstrates that very high levels of solvent can be trapped in the film if significant cure of the resins occurs before application of the coating. An advantage is seen here for PM, since high residual solvent levels may be expected to cause inferior chemical and water resistance or changes in flexibility or blocking resistance overtime as the residual solvent is very slowly released.

Two advantages in the substitution of glycol ethers for

glycol ether esters in two-component urethane coatings are obvious. First, the glycol ethers are necessarily less costly than the analogous esters. Second, a glycol ether such as PM has a faster evaporation rate than the acetate ester and is therefore not trapped in the cured films to the same extent as any of the ester solvents.

The dominant consideration in the selection of a glycol ether solvent is, of course, that the relative rates of reaction of the glycol ether and the polyol with the isocyanate resin be sufficiently dissimilar. Specifically, the ratio of rate constants $k_{polyol}/k_{solvent}$ should be substantially greater than 1. Otherwise, the growing polyurethane chains will be terminated by the monofunctional solvent, adversely affecting the outstanding chemical and physical properties typical of polyurethane films (Equation 3). The secondary

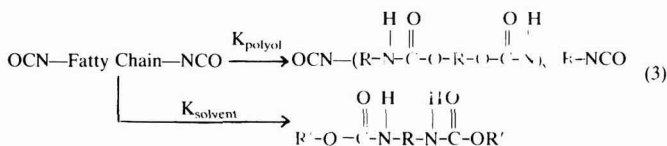


Table 6
Clear two-component urethane coating

Part A	lbs
Polyester Polyol Resin C	24.3
PMA or PM	5.0
Dibutyltin Dilaurate Catalyst (1% in MEK)	0.1
Part B	
Isocyanate Resin B	18.1
PMA or PM	2.0

hydroxyl nature of propylene-based glycol ether solvents will to some extent obviate this concern with PM and PTB. This study confirms earlier work which has shown secondary hydroxyls to be a factor of 3 less reactive than primary hydroxyl. Also, the steric constraints associated with the hydroxyl group of PTB further diminishes its reactivity. As some reaction of, for example, PM with isocyanate resin will necessarily

Impact Resistance

Pot Time. Hrs	%NCO		Sward Hardness (8 Day Cure)		(D/R) (8 Day Cure)		%Solvent In Film (wt%)	
	PMA	PM	PMA	PM	PMA	PM	PMA	PM
0	6.5	6.5	54	50	115/130	115/155	0.4	0.2
1	6.2	6.2	56	46	150/130	>160	0.7	0.3
2	6.1	5.7	42	40	>160	>160	1.0	0.4
4	5.9	5.4	—	—	—	—	—	—
5	5.5	5.2	32	24	>160	>160	3.7	0.9
24	1.5	1.3	—	—	—	—	—	—
72	0.1	0.1	—	—	—	—	—	—

Gellation at 5 - 5.5 MPS in PIVIA, 8.5-1 MPS in PIVI

occur, the pot life of a PM containing formulation may be diminished relative to that of a glycol ether ester containing formulation. Formulations with PM must therefore be more closely monitored than those with PMA or EEA to avoid the detrimental effects of the PM-isocyanate reaction.

A common problem with ambient-cure urethane coatings is release of solvent from curing films. The rapid rate of the crosslinking reactions in a two-component system competes with the rate of solvent diffusion through the polymer film. As a result solvents may be trapped in a cured film and only slowly released over a period of weeks or months. A somewhat more rapidly evaporating solvent such as PM will tend to escape the curing film before being trapped to any significant extent. This behaviour has been demonstrated for a wide variety of solvents

including esters, ketones, glycol ethers and glycol ether esters. Results of poor solvent release include diminished chemical and water resistance, low gloss and distinctness of image, increased (but varying) flexibility and softer films. Solvent retention is affected primarily by the neat solvent evaporation rate and frequently by steric factors which influence solvent diffusion rates through polymeric films. thus, slower evaporating and highly branched solvents will be more highly retained. For example, n-butyl acetate is only slightly retained in urethane coatings while diethylene glycol ethyl ether acetate retention is high. Also, isobutyl isobutyrate release is significantly slower than would be predicted from its neat solvent evaporation rate. The work reported here is consistent with these earlier observations in that PM is relatively released from curing films and the branched PTB is retained at fairly high levels.

Summary

This work has demonstrated that certain glycol ethers such as propylene glycol methyl ether can be used effectively as a solvent for air-drying two-component polyurethane coatings. The reactivity of ethylene-based glycol ethers with isocyanate resins which prohibit their use in the same systems is sufficiently diminished with the secondary hydroxyl group of PM to allow its use in these coatings. The higher evaporation rate of PM relative to the glycol ether esters gives the additional advantage of improved solvent release and consequently harder and more resistant films.

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Continued from p.314

Table 7

Ball Mill Formulation	Conventional millbases (%)		Solsperse millbases (%)			
40% resin solids solution	90	90	—	—	—	—
10% resin solids solution	—	—	70	70	60	70
Solsperse 24000	—	—	10	15	13.3	15
Solsperse 5000	—	—	—	—	5	6.7
Color Black FW 200 (Degussa)	10	—	15	15	—	—
Black Pearls 1300 (Cabot)	—	10	—	—	20	15

has a dramatic effect on millbase viscosity, reducing the thixotropy. As a result the finished paint has better flow (absence of orange-peel), higher gloss, and much higher intensity or jetness, a feature which is very appealing in black automotive finishes. Maximum jetness is seen when the synergist is utilised but it may be excluded if the effect on shade is unacceptable.

Summary

The above examples provide some insight into the numerous benefits of using Solsperse hyperdispersants. This new technology

represents a scientific approach to pigment dispersion and can be used to solve some of the more difficult problems of dispersing pigments and of making higher quality paints.

However using Solsperse hyperdispersants is not foolproof; care is needed to select the correct hyperdispersant for the pigment and solvent system, and it is essential to use the correct quantity to satisfy the surface-area of the pigment.

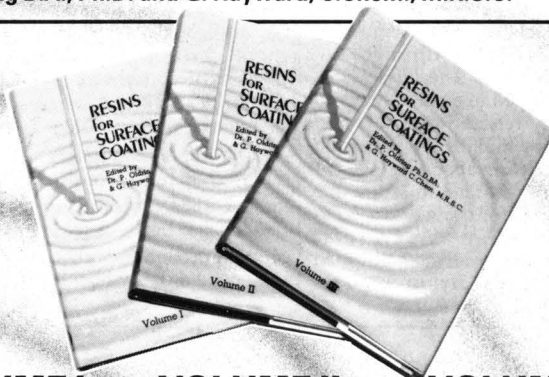
So to return to the title of the article, who needs wetting agents now that Solsperse hyperdispersants are available? ■

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The effect of the chemical composition of unpigmented organic coatings on the corrosion protection of steel

Part 2: Evaluation of heat-cured coatings made from the modified epoxy resins

D. E. A. Williams-Wynn, Department of Applied Chemistry, University of Natal, King George V Avenue, Durban, South Africa

Abstract

Coatings based on terminally modified epoxy resins, which had been cross-linked with urea-formaldehyde resins, were generally too brittle for normal use and failed by cracking and the concomitant corrosion of the steel substrate when exposed under typical service conditions. The water resistance of these coatings was excellent in static tests; thus they performed well as a barrier to electrolyte penetration as assessed by AC or DC electrical measurements, implying excellent corrosion protection. Partial esterification of the hydroxyl groups in the modified resin molecules produced base resins which when cross-linked produced tough flexible adhesive films with greater water repellency and good electrical properties.

Phosphate pretreatment of the steel substrates improved the corrosion resistance of all coating systems, yet electrical and especially AC impedance measurements suggested that this combination was less satisfactory than when the coatings were applied to bare metal. The proper selection of test procedures is therefore critical when evaluating novel coatings.

Introduction

Traditional methods for the evaluation of corrosion protection have tended to rely on accelerated weathering ('weatherometer') tests – sometimes more appropriately referred to as artificial weathering tests – condensing humidity and salt spray exposure. With modern coatings the correlation between predicted performance from the above test procedures and actual performance has become weaker and unreliable¹⁻⁵. Moreover if the coating systems are effective some of these tests require up

to 1000 hours to complete and this is unacceptably long for development work, and delays and restricts progress considerably. Nevertheless this type of test, and especially the ASTM salt spray test⁶, is frequently specified because of the vast experience of this technique and the lack of an acceptable alternative for testing anti-corrosion coatings. Thus in this investigation many of the tests listed in the plan of the experiment were included to characterise the coatings using conventional methods.

Many workers have emphasised the importance of measuring the electrolytic resistance of paint films during the investigation of the corrosion of metals beneath protective surface coatings. This general subject has been reviewed by Hartley⁷ and by Leidheiser⁸. Of the various new techniques which have been used in recent years, AC impedance enjoys current popularity; the use of impedance measurements for the evaluation of protective non-metallic coatings has been reviewed⁹. The advantage of the application of AC impedance to the measurement of corrosion under paint films has been summarised¹⁰. A DC procedure for determining the permeability of paint films by aqueous electrolyte recently published¹¹, overcomes the objections that applied current can introduce extraneous reactions and/or can accelerate corrosion rates. However, Mills claims¹² that DC measurements can be made with as small a perturbing voltage as the AC impedance method uses.

The measurement of adhesion is a contentious subject¹³, but adhesion is an important property of a protective coating. Thus to characterise the experimental coating systems two methods for determining adhesion were included in the test regime, namely the ASTM technique for measuring

adhesion by tape test¹⁴, and the Hesiometer knife-cut test¹⁵. The latter test was used under various environmental conditions since the ability of a coating to maintain good adhesion under wet conditions is thought to be very important with respect to its ability to provide corrosion protection^{12, 16, 17}.

The physical and mechanical properties of a cured coating are linked to the nature of the polymeric material under the conditions of use or exposure. Thus a knowledge of the glass transition temperature (T_g) of the coatings, and their hardness under various conditions, i.e. in the glassy or rubbery state, may be of value in interpreting observed performance in the tests. Since the measured value of the glass transition temperature varies depending on the methods of determination, the T_g was obtained using both thermo-mechanical¹⁸ and thermal methods (differential scanning calorimetry). Hardness was measured using microindentation methods^{18, 19}, and acoustic emission studies²⁰ were used to evaluate the stress/strain performance of a selection of the coatings. The results of the acoustic emission studies have been published separately²¹.

Experimental

The two series of modified and esterified epoxy resins, the preparation of which was described in Part 1, were blended with a urea-formaldehyde (UF) resin (butylated dimethylolurea type) and thinned to 4-5 poise with 4-methyl-2-pentanone (MIBK). These coating formulations, in which the mass ratios of experimental resin to crosslinker were 4:1, were applied by spinning to vapour degreased mild steel panels (1 mm Pyrene Gold seal lished, process 8711) and to prebaked Bonderite phosphate process 134 steel panels. Cure was affected by stoving at 165°C for 30 minutes to crosslink the coating. Compatibility problems were experienced with the higher levels of esterification (resins B2, B4, B7 and B8) and this led to substitution of the UF resin by a butylated melamine-formaldehyde (MF) resin in these cases. The average coating thickness was of the order of 40µm.

Resins used for coatings

A Modified epoxy resins

A1: tall oil fatty acid modification of Epikote 1004.

A2: *p-tert*-butyl benzoic acid modification of Epikote 1004.

A3: *p*-*tert*-butyl phenol modification of Epikote 1004.
A4: *p*-phenyl phenol modification of Epikote 1004.
A5: diethanolamine modification of Epikote 1004.
A6: diphenylolpropane modification of Epikote 800.

B Esterified/modified epoxy resins

B1: resin A2 esterified with 2 moles of tall oil fatty acid.
B2: resin A2 esterified with 4 moles of tall oil fatty acid.
B3: resin A3 esterified with 2 moles of tall oil fatty acid.
B4: resin A3 esterified with 4 moles of tall oil fatty acid.
B5: resin A5 esterified with 2 moles of tall oil fatty acid.
B6: resin A5 esterified with 4 moles of tall oil fatty acid.
B7: resin A5 esterified with 6 moles of tall oil fatty acid.
B8: resin A5 esterified with 8 moles of tall oil fatty acid.

Test procedures for coated panels

The schedule of tests adopted to assess the performance of the coatings was as follows:

R Exposure tests

R1: accelerated (artificial) weathering.
R2: continuous condensing humidity.
R3: salt spray.
R4: exterior exposure: Slough and Durban.

R1 Accelerated weathering: Suitably edged and backed panels were exposed for a maximum of 1000 hours in a Marr artificial weathering machine with a 1600 watt enclosed carbon arc and operating cyclically: 10 hours wet, 2 hours dry. Panels were examined after 100 hours, 250 hours, 500 hours and at the end of the test.

R2 Continuous humidity: Edged and backed panels were assessed for their resistance to humidity under condensing conditions. The atmosphere within the cabinet was maintained at 100% rh with the temperature cycling between 42 and 48°C. The test was continued for 1000 hours with intermediate inspections as above.

R3 Salt spray: Suitably edged and backed panels, scored through the coating using a 1 mm drill bit set to cut at least 10 μ m into the steel for a length of about 80 mm, were exposed to a continuous fog of 5% sodium chloride solution at 33 to 36°C (ASTM B117-73). The panels were inspected after four

time intervals as above.

R4 Exterior exposure: Suitably backed panels scored through the coating, as for the salt spray test, were exposed for three summer months on the roof of a building in Slough at an angle of 45°, facing south. This site has a temperature, industrial atmosphere. Similar panels were exposed for six months on the roof of the Applied Chemistry Department, University of Natal, Durban, South Africa, which has a sub-tropical, marine, industrial atmosphere.

S Water permeability tests and corrosion monitoring

S1: DC conductivity measurements.
S2: AC impedance measurements.

S1 DC conductivity measurements were made using the apparatus and the simple pulse method previously described¹¹. The coated surfaces of the metal panels were contacted with electrolytes consisting of 0.5 or 1.0 M sodium chloride solutions in which the platinum electrode was immersed. Initial measurements were made immediately; measurements were repeated at intervals whose length was determined by the rapidity of change in the paint film conductivity. If it is assumed that the film resistivity is inversely proportional to the quantity of electrolyte which has permeated into the coating, these measurements give an indication of the effectiveness of the barrier nature of the coating.

S2 AC impedance measurements were made using the technique previously described¹⁰. Most of the results were obtained using a tangential impedance monitor, but a few measurements were made with a frequency response analyser.

The variation of the impedance and its components as a function of frequency are generally displayed as Nyquist and/or Bode plots. The different stages in the corrosion of metal under paint can be related to various features of these plots and for convenience a somewhat arbitrary but useful classification of five periods in the lifetime of the test panels has been recognised¹⁰.

Bode plots are convenient and simple to calculate and display manually, and interpretation is relatively straightforward; Nyquist plots are more complex, thus Bode plots ($\log |Z|$ vs $\log f$) were chosen to illustrate the results in this study and from which the performance of the coatings when

immersed in aqueous electrolyte (3% sodium chloride solution) could be assessed.

The five periods are identified as:

1. The initial or passive period in which the corrosion rate is very small or zero and the water content of the coating is low. The Bode plot is a straight line of slope -1 and the impedance at $\log f=0$ is extremely high ($>10^9$ ohm).

2. The transitional period (during which there is no visible deterioration). The Bode plot is mainly a straight line of slope -1 but the line decreases in slope as the frequency decreases. The impedance at $\log f=0$ is lower, approaching 10^7 ohm.

3. The semi-circular period (referring to the shape of the Nyquist plot) in which there is a distinct break in the slope of the Bode plot forming a plateau at which the impedance values at $\log f=0$ vary between 10^4 and 10^7 ohm. A significant quantity of water is distributed in the film.

4. The diffusion period in which corrosion has started and is visually evident. The curve of the Bode plot consists of three sections: At high frequencies the slope of the line is -1 , a mid-section plateau, and a low frequency slope of $-1/2$. The impedance at $\log f=0$ is typically between 10^3 and 10^5 ohm.

5. The active period in which corrosion is very active and obvious. A variety of different corrosion processes are clearly visible. The Bode plot is irregular.

For the purpose of determining when the coating was deemed to be no longer protective, i.e. blistering, partial film detachment and/or visible corrosion, an impedance value of $\log |Z|=1$, represented by the plateau on the Bode plot in period 4, was taken as the limit.

The time required to reach this value was estimated for each of the coatings on both mild steel and phosphated steel panels, after normal conditioning and after weathering in the Marr accelerated weathering equipment for 150 hours.

T Adhesion

T1: hesiometer, wet and dry.
T2: cross-cut, dry conditioned film.

T1 Hesiometer knife-cut test: The instrument used was of the type designed by W. K. Asbeck, et al²². The test¹⁵ measures the force in kgf,

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required to strip a coating from its substrate when a 6.35 mm wide 30° tungsten carbide cutting tool travels along the lathe bed of the instrument. Tests were made on dry conditioned films and on films which had been in contact with liquid water for 14 days.

T2 Cross-cut tape test: The conditions and procedures laid down in ASTM D 3359-78, Method B¹⁴, using 1 mm spacings for the lattice pattern, were applied.

U Film hardness and glass transition temperature:

U1: Hardness by ICI microindentation tester.

U2: Hardness by Tukon microhardness tester.

U3: T_g by differential thermal analysis.

U4: T_g by microindentation, dry and soaked.

U1 ICI microindentation hardness was measured using a pneumatic hardness tester¹⁸ which can operate at any desired temperature between -14°C and 90°C. The spherical indenter used had a diameter of 0.4 mm and was applied at a load of 4 g. Measurements were made of the depth of indentation after 2 minutes of applied load, with a limiting value of 6 μm. Having calculated the T_g of the films the relative hardness of the films at the T_g and at T_g-5 and T_g+5 were determined.

U2 Knoop indentation hardness was measured using a Tukon microhardness tester¹⁹ fitted with the Knoop indenter²³ and operated in the standard atmosphere. A dead-weight load of 25 g was applied to the indenter which was in contact with the coating surface for 45 seconds. Results are quoted as Knoop Hardness Number (KHN).

U3 Glass transition temperature by differential thermal analysis was measured using a Perkin-Elmer model DSC-1 differential scanning calorimeter.

U4 Glass transition temperature by microindentation was measured using the ICI pneumatic hardness tester (see U1). This thermomechanical method is time-dependent and the results are likely to vary from results obtained by thermal methods such as DSC.

Results

R Exposure tests

R1 Accelerated (artificial) weathering: After only 100 h of exposure

several of the coated panels were showing defects such as microblistering, water spotting and incipient corrosion. Water sensitivity which resulted in hazy or dull films was independent of the substrate. Corrosion was limited to the mild steel panels except where the film was severely disrupted as in the cracking of the excessively brittle film based on the diethanolamine modified Epikote 1004 resin. Microblistering was not completely independent of the substrate; the incidence was greater on the mild steel panels than on the Bonderite panels.

Many of the experimental finishes had shown no apparent defect at this stage. It is not possible to ascribe the resistance to deterioration to chemical composition but there are indications that resins containing ether links in the modified epoxy resins are more durable. These however are rather brittle and the incorporation of a small amount of long chain fatty acid into the molecule gives a resistant coating despite the introduction of ester groups. The high levels of esterification produced finishes which were more sensitive to and were adversely affected by accelerated weathering.

After 250 h of exposure to accelerated weathering the finishes based on resins with ether links were free of obvious defects. In addition the resins containing low levels of esterified tall oil fatty acids were still performing satisfactorily on mild steel. However, the superior performance of the phosphate pretreated panels under the more easily degraded coatings was clearly evident at this stage.

Early breakdown (<500 h) is generally limited to the finishes based on the modified resins which failed by cracking. Low level of esterification of the modified resins with tall oil fatty acid introduced internal plasticisation and a considerable lowering in the glass transition temperature of the coatings made from them. These coatings were much more protective to the limit of the test at 1000 h. Higher levels of esterification of the modified resins produced soft, less protective coatings which failed by blistering and underfilm corrosion.

R2 Continuous condensing humidity showed that some of the coatings were very water sensitive, the effects ranging from yellowing through hazy to milky. Early failure (<100 h) occurred with the diethanolamine modified epoxy resin; with increasing esterification with tall oil fatty acids water sensitivity decreased. On prolonged exposure the cloudy films had wrinkled and cracked

indicating swelling through water imbibition. The high water absorption of the coatings did not necessarily result in corrosion of the metal substrate.

Modifications of the epoxy resins involving ether links resulted in coatings which were water resistant although brittle, and corrosion of the substrate metal was mainly limited to the areas where the film had cracked. Esterification of the modified resins eliminated cracking of the coatings and maintained excellent water resistance. But high levels of esterification resulted in soft films which tended to blister.

R3 Salt spray tests caused minimal early attack on the metal but finishes based on the resins containing ester groups showed some blistering and film detachment. With extended exposure to salt spray extensive blistering occurred around the scribe with varying degrees of rust creep on mild steel whereas the performance on phosphated steel was excellent.

Limited esterification of the modified resins containing ether groups produced films which did not crack during the salt spray tests and these coatings were protective to mild steel with little blistering and minimal rust creep. The higher levels of esterification caused a greater tendency to blister formation and film detachment with consequential underfilm corrosion. On the phosphate pretreated metal the coatings based on resins with low levels of esterification had not blistered and had prevented underfilm corrosion except for about 3 mm of rust creep after 1000 h in salt spray.

R4 Exterior exposure: Three months exposure at Slough caused extensive deterioration on control panels but the coatings based on the experimental resins were very protective provided the films were not excessively hard and brittle. The brittle films tended to crack on exposure and the exposed metal, whether phosphate pretreated or not, was readily attacked with general rusting. Where the films were intact there was little or no blistering or rusting on either substrate.

The incidence of cracking was greatly reduced when the coatings were based on the modified resins which had been internally plasticised by esterifying with tall oil fatty acids. The low levels of esterification produced the best results. The higher levels of esterification produced the softer films which dulled on exposure and also permitted the blistering and some underfilm corrosion.

Table 1

Time in hours for electrolyte to saturate the coating film as determined by the change in DC resistance measurements

Coating	Electrolyte Concentration			
	0.5 M		1.0 M	
	Steel 8711	Bond 134	Steel 8711	Bond 134
A1 TOFA/Epikote 1004/UF	NC	NC	250	NC
A2 PTBBA/Epikote 1004/UF	NC	50	NC	200
A3 PTBP/Epikote 1004/UF	NC	10	NC	30
A4 PPP/Epikote 1004/UF	NC	50	NC	50
A5 DEA/Epikote 1004/UF	NC	80	NC	NC
A6 BPA/Epikote 880/UF	30	100	40	40
B1 2 TOFA/A2/UF	NC	NC	NC	200
B2 4 TOFA/A2/MF	NC	350	NC	350
B3 2 TOFA/A3/UF	NC	190	NC	140
B4 4 TOFA/A3/MF	NC	NC	NC	NC
B5 2 TOFA/A5/UF	NC	60	NC	NC
B6 4 TOFA/A5/UF	NC	NC	NC	NC
B7 6 TOFA/A5/MF	NC	NC	NC	NC
B8 8 TOFA/A5/MF	NC	80	NC	NC

Note: NC=no significant change in the electrical resistance curve for the coating during the 1500 h duration of the test. Thus these films had not been saturated with electrolyte.

TOFA=tall oil fatty acid, PTBBA=*p-tert*-butyl benzoic acid, PTBP=*p-tert*-butyl phenol, PPP=*p*-phenyl phenol, DEA=diethanolamine, BPA=diphenylol propane A).

Three summer months exposure in Durban produced surprisingly little deterioration; only two of the coating systems had cracked. The softer coatings showed poor superficial weathering but were still protective to the metal beneath. Thus the coatings which were based on the modified epoxy resins, and those that had been esterified to the lowest levels were still glossy, and bright metal could be seen through the clear films.

After six months exposure in Durban dramatic changes had occurred since many panels were extensively and seriously corroded with catastrophic failure of some coatings. The brittle films had cracked and crazed with associated corrosion. Internal plasticisation eliminated the tendency to crack but higher levels of esterification were needed to achieve this in this test compared with the accelerated tests.

It is interesting that in the natural exposure tests there is no clear cut preference for the modifications involving ether linkages compared with ester linkages.

S Water permeability tests and corrosion monitoring

S1 DC conductivity measurements: This technique, as is the case with all

tests involving the measurement of electrolytic resistance, is dependent on defect-free films. However, since relatively small areas of the coated panels are included in the cell, it is significantly more easy to find suitable areas for measurement than when the

Table 2

Log resistance of coating films after 750 h exposure to electrolyte as determined by DC resistance measurements

Coating	Electrolyte Concentration			
	0.5 M		1.0 M	
	Steel 8711	Bond 134	Steel 8711	Bond 134
A1 TOFA/Epikote 1004/UF	8.95	10.60	6.55	10.85
A2 PTBBA/Epikote 1004/UF	9.45	<6	10.40	<6
A3 PTBP/Epikote 1004/UF	6.10	<6	7.80	<6
A4 PPP/Epikote 1004/UF	8.20	<6	9.55	<6
A5 DEA/Epikote 1004/UF	10.10	<6	<6	<6
A6 BPA/Epikote 880/UF	8.75	<6	9.15	8.90
B1 2 TOFA/A2/UF	10.50	8.50	11.30	<6
B2 4 TOFA/A2/MF	<6	7.70	11.15	7.40
B3 2 TOFA/A3/UF	10.95	7.15	11.00	7.75
B4 4 TOFA/A3/MF	8.00	11.00	11.30	11.00
B5 2 TOFA/A5/UF	10.45	9.95	11.00	10.05
B6 4 TOFA/A5/UF	10.30	10.70	11.00	10.80
B7 6 TOFA/A5/MF	9.60	10.35	10.85	10.65
D8 8 TOFA/A5/MF	11.00	10.75	11.00	11.00

TOFA=tall oil fatty acid, PTBBA=*p-tert*-butyl benzoic acid, PTBP=*p-tert*-butyl phenol, PPP=*p*-phenyl phenol, DEA=diethanolamine, BPA=diphenylol propane A).

whole panel is under test. Nevertheless some scatter is noted in the results which are summarised in Tables 1 and 2. These values were derived from the graphical representation of the results of resistance with time. Typical graphs are shown in our paper¹¹.

Since the resistance of the paint coating was dependent not only on the concentration of the electrolyte with which it was in contact but also on the nature of the polymer used for the coating, no single value for resistance could be used in determining 'failure' by penetration of electrolyte. In many cases the period of the test (1500 hours) was not sufficiently long for the resistance to reach a limiting value. Thus neither limiting value nor the time required to reach that value could be quoted as performance parameters for these coatings. In many graphs a significant change in the slope of the resistance-time curve was noted. The times required for this change of slope to occur are given in Table 1. In some instances the absorption of water, as inferred by the continuing decrease in the measured resistance, persisted to the end of the test period and no inflection in these curves was noted.

In Table 2 the values are given for the resistance of the coating films after 750 h of contact with the electrolytes.

It is clear that absence of a time value for any given coating under a particular set of circumstances does not

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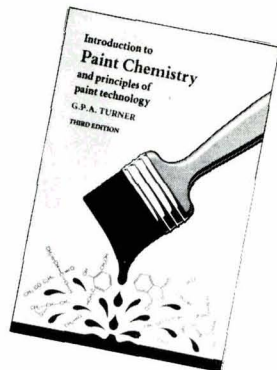
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necessarily mean a defective film. More likely, as shown in Table 2, the resistance of the coating had remained so high that no significant change in resistance had taken place during the test of more than 1500 hours.

Despite the variability and inconclusive nature of some of the results, certain general observations can be made. In the first place the higher concentration test medium (1.0 M sodium chloride) penetrated and saturated the coating films more slowly than the 0.5 M sodium chloride solution. Secondly, the nature of the substrate appeared to affect the results, penetration of the electrolyte being more rapid and the fall in resistance being greater for those coatings applied to phosphate pretreated steel than to mild steel. Thirdly, many of the experimental coatings have excellent resistance to electrolyte penetration; this is shown by the very high electrical resistances which many of these coatings exhibit even after 750 h contact with the electrolyte, and the insignificant changes in conductivity these coatings underwent despite the long duration (1500 h) of the test.

S2 AC impedance measurements: The data for this assessment are presented in Table 3. The tests were made with fairly large areas of the coated panels exposed to the electrolyte. Thus coating defects were a problem but the effects of the defects could be neutralised by spot-sealing with wax. This reduced the variability and significant trends can be

seen. Phosphate pretreatment tended to reduce the impedance of the unweathered coatings especially those producing brittle films. The tough, and even the unacceptably soft coatings, were uniformly resistant to electrolyte penetration.

Pre-weathering of the panels prior to testing greatly reduced the protection afforded by the harder coatings especially on mild steel; phosphate pretreatment of the steel generally improved the performance of the coatings. The softer film made from the long-chain fatty acid modified epoxy resin was protective even after four months of exposure to simulated sea water. Plasticisation of the hard and brittle resins by partial esterification with tall oil fatty acid also resulted in excellent performance as assessed by AC impedance measurements.

T Adhesion

T1 Hesiometer knife-cut test: It is generally accepted¹³ that a value of 1.0 kgf on the apparatus used is satisfactory for good adhesion in practice, but a value of 1.2 kgf is recommended as the minimum for dry adhesion.

The most obvious and consistent results were the low values for adhesion of the films to the Bonderite 134 phosphate pretreated panels compared with mild steel panels. This is contrary to what was expected but the explanation lies in the limiting strength

of the spicular phosphate layer which has a value of about 1.4 kgf. The good results obtained on steel ranged between 2.0 and 4.3 kgf.

Some of the hard, brittle coatings had excellent adhesion to steel (approximately 2.5 kgf) but the best results were obtained with the tough films formed with the lightly esterified, internally plasticised resins (approximately 3.0 kgf). Higher levels of esterification, which gave the softer, more flexible films resulted in apparently lower adhesion, but the failure in these cases was usually due to low cohesive strength.

Tests which were made on coatings which had been in contact with liquid water for 14 days showed that the adhesion of some water wet films was very poor. Sometimes the whole coating lifted from the substrate and in these cases phosphate pretreatment was of no benefit. The best results were again shown by the tough films incorporating the resins with a low level of esterification. The adhesion to steel was reduced only marginally from 2.8-3.0 kgf to 2.6-2.8 kgf, as, for example, the coatings based on resins B1 and B3.

T2 Cross-cut tape test: Even with a 1 mm lattice many coatings had a perfect score (grade 5) yet there was considerable variation in adhesion as assessed by the Hesiometer. The most obvious discrepancy between the two tests was the assessment of adhesion of the coatings to the phosphate pretreated panels for which the results of the cross-cut tape test were invariably good.

Another area where the cross-cut test failed to be discriminating was the consistent high scores for the excessively soft films with poor cohesive strength.

U Film hardness and glass transition temperature

U1 Hardness by ICI microindentation tester: At temperatures higher than the glass transition temperature ($T_g + 5$) many of the coatings were too soft for measurement by this instrument, but these were generally based on the highly plasticised resins, which in any case were unsatisfactory coatings at room temperature. The tough protective coatings had micro-indentation hardness values of between 0.6 and 0.7 μm at room temperature, but a significant softening occurred at the glass transition temperature. This is shown in Table 4 for the coatings based on resins B1 and B3.

Table 3

Time in hours to reach the diffusion period and onset of underfilm corrosion as determined by AC impedance measurements

Coating	Original		Weathered	
	Steel	Bond	Steel	Bond
A1 TOFA/Epikote 1004/UF	3000	>3000	>2000	>2000
A2 PTBBA/Epikote 1004/UF	700	>3000	4	>2000
A3 PTBP/Epikote 1004/UF	>3000	600	>2000	360
A4 PPP/Epikote 1004/UF	1600	1400	4	100
A5 DEA/Epikote 1004/UF	1500	1000	0	0
A6 BPA/Epikote 880/UF	>3000	2000	6	>1500
B1 2 TOFA/A2/UF	>2000	>2000	>2000	>2000
B2 4 TOFA/A2/MF	>2000	2000	300	1500
B3 2 TOFA/A3/UF	>2000	>2000	1500	>2000
B4 4 TOFA/A3/MF	2000	2000	2000	1200
B5 2 TOFA/A5/UF	1600	>2000	>2000	>2000
B6 4 TOFA/A5/UF	>2000	>2000	>2000	>2000
B7 6 TOFA/A5/MF	>2000	>2000	>2000	>2000
B8 8 TOFA/A5/MF	>2000	>2000	>2000	>2000

TOFA=tall oil fatty = *p*-*tert*-butyl benzoic acid, PTBP=*p*-*tert*-butyl phenol, PPP=*p*-phenyl = diethanolamine, =diphenylol propane (Bisphenol A).

Table 4
Variation in microindentation hardness with temperature

Coating	Room Temp	At T _g -5	At T _g	At T _g +5
A2 PTBBA/Epikote 1004/UF	0.3	0.6	1.2	2.7
B1 2 TOFA/A2/UF	0.6	0.9	1.4	2.5
A3 PTBP/Epikote 1004/UF	0.2	0.4	1.3	3.6
B3 2 TOFA/A3/UF	0.7	1.5	1.9	3.1

Table 5
Effect on the level of esterification on the Knoop hardness of coatings on steel

Type of Resin	Level of esterification moles/mole				
	0	2	4	6	8
PTBBA Modified Epikote 1004	19.3	13.6	4.7	—	—
PTBP Modified Epikote 1004	19.4	11.3	6.4	—	—
DEA Modified Epikote 1004	19.3	8.9	2.1	1.6	1.3

Table 6
Effect on the level of esterification on the glass transition temperature, °C

Type of Resin	Level of esterification moles/mole		
	0	2	4
PTBBA Modified Epikote 1004	82	46	4
PTBP Modified Epikote 1004	81	50	14
DEA Modified Epikote 1004	73	48	6

Table 7
Effect of the level of esterification on the glass transition temperature, °C

Type of Resin	Level of esterification moles/mole		
	0	2	4
PTBBA Modified Epikote 1004	81	32	5
PTBP Modified Epikote 1004	75	32	12
DEA Modified Epikote 1004	74	30	-3

Also included in Table 4 are the hardness values for the unacceptably brittle coatings with indentation values of 0.2 and 0.3 μm at room temperature. At the glass transition temperature the hardness is similar to that of the coatings based on the plasticised resins but the T_g of the unplasticised coatings is about 50°C higher than the T_g of the plasticised coatings, see section U4.

U2 Knoop indentation hardness: Tukon hardness is quoted in Knoop hardness number for which low values represent soft films. With the exception of the coatings based on the tall oil fatty acid modified epoxy resin, with a Knoop value of 17.8, the modified resins gave coatings which were extremely hard with Knoop values in the range 19 to 21. When the modified resins which had been esterified with tall oil fatty acid

were incorporated into coatings the resulting films were significantly softer as shown in Table 5. Even when the lowest level of esterification was used, namely 2 moles of tall oil fatty acid/mole of resin, the hardness of the coatings formed was fairly low; higher levels of esterification produced unacceptably soft coatings.

An interesting side issue resulting from the measurement of Knoop hardness of coatings on steel was the lower values for films on the phosphate pretreated steel panels compared with the hardness of the same coatings on Steel 8711. The differences are between 0.5 and 2.5 in Knoop hardness number.

U3 Glass transition temperature (DSC): With the exception of the coatings based on the tall oil fatty acid

modified epoxy resin, all of the coatings made from the unesterified modified resins had high T_g values which varied between 70 and 90°C. Conventional coatings for steel have T_g values of the order of 50°C.

Esterification of the experimental resins produced coatings with considerably lower T_g values as shown in Table 6. In fact glass transition temperatures could not be measured on the coatings made from highly esterified resins using thermal analytical techniques since the T_g values were below the lower limit of the instrument.

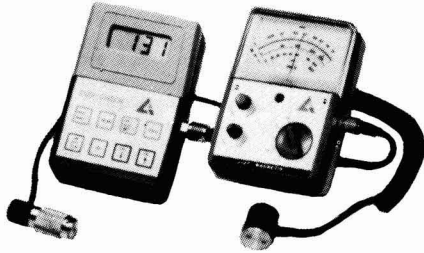
Esterification of the modified epoxy resins with two moles of tall oil fatty acid/mole of resin has resulted in coatings with glass transition temperatures of the same order as those of the conventional coatings, ~50°C.

U4 Glass transition temperature by microindentation: The thermo-mechanical assessment has given T_g values slightly lower than those obtained by DSC but in general the results for T_g by microindentation, Table 7, follow the same pattern as that noted for T_g by thermal analysis, Table 6.

An advantage of the micro-indentation technique for determining T_g is that the measurements can be made under a variety of environmental conditions. Normally the measurements of T_g are made under anhydrous conditions; specimens are conditioned in the cabinet in which the measurements are made with P₂O₅ as the desiccant. This not only ensures consistent conditions of test but also protects the sensitive equipment from corrosion. However for limited periods the conditions can be altered and in this experiment the specimens having been measured dry were soaked in distilled water for ten days and microindentation measurements made over a range of temperatures on the coatings after blotting dry. The P₂O₅ was removed from the cabinet and replaced with wet filter paper to minimise the loss of water from the film during the measuring period. The change in T_g on soaking gives a measure of the degree of plasticisation provided by the imbibed water.

The change in T_g due to soaking depends on the chemical nature of the coating. Those films which other tests have shown to be hydrophilic show a marked decrease in glass transition temperature on soaking. For example, the ΔT_g of the coating from the diethanolamine modified epoxy resin

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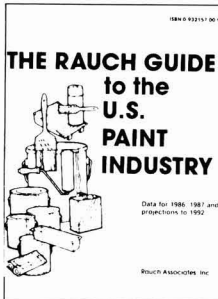
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Table 8

Effect of the level of esterification on the change in glass transition temperature on soaking, °C

Type of Resin	Level of esterification moles/mole		
	0	2	4
PTBBA Modified Epikote 1004	30	5	3
PTBP Modified Epikote 1004	23	7	5
DEA Modified Epikote 1004	36	18	—

was 36°C, whereas the hydrophobic coatings showed changes in glass transition temperature on soaking of only about 4°C.

The introduction of the tall oil fatty acid moiety into the modified resins imparted not only a plasticising effect but also an increased resistance to hydration. Thus the change in T_g of the coatings based on the esterified resins due to water absorption is small, of the order of 5°C, see Table 8.

Discussions and Conclusions

Effect of Phosphate Pretreatment

The phosphate pretreatment of the steel had the predictable result of improving the corrosion resistance of coated metal when exposed to various 'weathering' tests. Thus although most of the experimental coatings gave ample protection to the metal substrate when specimens were exposed in a Marr artificial weathering machine, phosphate pretreatment prevented corrosion of the metal in those few cases where the coatings failed. When the coated panels were subjected to continuous condensing humidity (a much more rigorous test than artificial weathering) there was rapid development of black spot underfilm corrosion with some of the coatings on steel. This was almost completely prevented by the use of the phosphate pretreatment even on prolonged periods of exposure.

In the ASTM salt spray test the hard, brittle coatings on steel failed early by blistering and cracking, with associated corrosion, but the phosphate pretreatment eliminated blistering and reduced the incidence of cracking. Thus the coated Bonderite panels withstood 1000 h in the salt spray, and corrosion occurred only where the films had cracked with very limited rust creep. Similarly, phosphate pretreatment of the steel greatly improved the performance of all coated panels exposed to the atmosphere whether in temperate Britain or in sub-tropical Durban.

Knoop hardness numbers for the coatings were found to be significantly

lower when the Tukon micro-indentation hardness was determined on the films on phosphate pretreated steel than on bare steel. Phosphate pretreatment also seemed to adversely affect the adhesion of the coatings when this was determined by the Hesiometer knife cut test. This is contrary to what was expected and the explanation of the apparent anomaly is that the knife cut through the phosphate layer since zinc phosphate crystals remained adhering to the undersurface of the detached films. Thus the cohesive strength of the phosphate layer must have been lower than the adhesion of the coatings to the substrates. Phosphate pretreatment had little effect on the adhesion classification of the films when the ASTM cross-hatch tape test was used, because this test is not sufficiently discriminating when adhesion is good.

The electrical conductivity of the films when immersed in an electrolyte was greatly increased when the coatings were applied to phosphate pretreated steel rather than to bare steel. This implies that phosphate pretreatment had promoted the electrolyte penetration of the coatings and thus would be expected to accelerate corrosion, which exposure tests disprove. This anomaly questions the validity of conductivity or impedance tests for determining the protection of steel by coatings.

Effect of Chemical Composition of Coating Resins

Epoxy resins were modified²⁴ to introduce into the resin molecule terminal groups which, when the resins were cross-linked into a coating, would be pendent from the backbone chain and thus influence the packing of the molecules. Also, these modifications introduced either ester or ether links which are known to behave differently when the organic coatings are exposed to electrolytes especially under warm, humid conditions. These modifications of the epoxy resins resulted in the introduction of additional hydroxyl groups into the molecules with increased potential for cross-linking as well as improved adhesion to steel.

However, the coatings produced by cross-linking the terminally modified resins tended to be hard and brittle, and in some cases sensitive to water. To reduce OH-group activity and to introduce a degree of plasticisation, a selection of the modified epoxy resins was partially esterified with tall oil fatty acid. These resins produced softer, more elastic coatings on cross-linking with urea-formaldehyde or melamine-formaldehyde resins.

The hard, brittle films were extremely hard as determined by micro-indentation tests at ambient temperature. Since the glass transition temperatures of these coatings were very high (>70°C) the coatings were in the glassy state at room temperature. Plasticisation of the coatings by esterifying the resins from which they were made produced films which were significantly softer due largely to the fact the T_g values had been reduced so much that at room temperature the coatings were in the rubbery state. When hardness was measured at the glass transition temperature, in each case the coatings made from the esterified (plasticised) resins were still significantly softer than those made from the unesterified modified resins presumably because the molecules of the latter were able to pack more closely than those of the former.

The influence of the resin type on performance is significant. The adhesion to steel of the finishes based on the modified epoxy resins varied considerably. The coatings based on the tall oil fatty acid modified Epikote 1004 (which were tough), and on the diethanolamine modified resins (which tended to crack) gave good results; the adhesion of the other finishes was fair to poor by both Hesiometer assessment or cross-hatch test. Wetting of the films by prolonged contact with water before testing did not materially affect adhesion except to slightly improve the adhesion of the very brittle coatings since the incidence of failures by chipping or cracking was reduced. The coatings formed from the resins with a low level of esterification which as a consequence were much less brittle but still tough, had excellent adhesion. This was little affected by water wetting. The removal of these coatings was by cutting; in reality a cohesion rather than an adhesion failure. The more highly esterified resins produced softer coatings with poorer adhesion, and a tendency to blister when contacted with water. In these cases failure was by peeling.

On exterior exposure most of the steel panels showed only a patina of rust under the hard brittle coatings formed by cross-linking the terminally modified epoxy resins. However, these coatings tended to crack and active corrosion occurred in the vicinity of the crack but with very limited rust creep. Cracking was eliminated by partial esterification of the resins used in the coatings without affecting the protection afforded the steel. Higher levels of esterification of the resins produced softer coatings which were not protective resulting in extensive under-film corrosion and rust creep. When subjected to laboratory exposure tests the brittle coatings tended to crack in the warm, humid environments but not in the artificial weathering test. The tough films gave excellent protection to the steel in all tests but the softer coatings failed by blistering and rust creep.

All of the coatings appeared to be resistant to penetration by electrolytes whether measured by DC resistance or by AC impedance. Thus these films were deemed to be protective by these assessments. The barrier effect is obviously excellent in these static tests where water imbibition may introduce a degree of plasticisation, but the brittle films fail under normal conditions of exposure.

Conclusions

The hard compact films produced by cross-linking the terminally modified resins by interetherification reactions with ureaformaldehyde resins were highly water impermeable and protected steel against corrosion almost indefinitely, provided they were not subject to stress. For example, cyclic temperature changes or flexing caused early failure of the coatings by cracking. Thus static tests of corrosion resistance by monitoring using for example AC impedance techniques are misleading. These coatings showed perfect resistance to electrolyte permeability for more than 3000 hours (the limit of the test) yet failed rapidly on ordinary exterior exposure.

Epoxy ester and epoxy ether resins produced from Epikote 1004 included a significant number of hydroxyl groups in the molecule which should have given good adhesion to steel. But adhesion failed by chipping and cracking and the very high OH-group content of the diethanolamine modified resins (10 OH-groups/molecule vs 6 OH-groups for the other terminally modified resins) also caused a degree of water-

sensitivity. Thus partial esterification of these hydroxyl groups not only reduced the water sensitivity but also introduced a degree of internal plasticisation to yield tough films without materially affecting adhesion. Extensive esterification with tall oil fatty acids resulted in excessively soft coatings with poor adhesion.

Thus as stated by Funke et al²⁵ there are still many unanswered questions relating to the protection of steel by organic coatings. Moreover, many of the test procedures traditionally used for the evaluation of coating systems and in fact some of the newer techniques for corrosion monitoring are indecisive at best and in some cases frankly misleading and contradictory.

This investigation involved the correlation of the composition and molecular geometry of the resin molecules used for coating steel with the performance of the coatings. Tough flexible adhesive films with excellent barrier properties to electrolytes can be made but the performance of the coatings is likely to be affected when pigments are incorporated into the formulations.

Acknowledgements

The author wishes to acknowledge with thanks, study leave granted by the University of Natal, the assistance given by AECI Paints, South Africa and the facilities provided by ICI (Paints Division) PLC.

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The Printing Ink Manual

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The Printing Ink Manual has an unrivalled reputation in the ink and printing industries as a comprehensive treatise on the development, manufacture and testing of printing inks. First published in 1961, on behalf of the Society of British Printing Ink Manufacturers, it has been continually updated in succeeding editions.

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The raw materials chapter gives detailed information on pigments, dyes, drying oils, resins, solvents and chemical additives together with data on materials for the increasingly important radiation curing systems.

The next five chapters on letterpress, lithographic, gravure, flexographic and screen printing inks are instructive for the student and informative for the experienced chemist and ink technician.

Throughout there is emphasis on practical aspects relating to ink formulation, performance on the printing machine and problem solving. Not surprisingly, considerable attention has been given to inks for the diversity of new substrates used in the packaging industries showing that ink and coatings developments have kept pace with the growth of these fields.

Radiation curable systems are now being more widely used. The chapter on this subject embraces

microwave, radio-frequency, infra-red, ultra-violet and electron beam curing processes. There is a well balanced review of the chemistry and technology of ultra-violet and electron beam curable inks and varnishes. The information on the fundamental chemistry of materials and reaction mechanisms in curing, is well presented. On the practical aspects, ink formulation principles, printing applications and types of radiation equipment are adequately described.

Throughout the chapters there are comments on the likely future trends and there is also a section on inks for special purposes e.g. inks for non-impact printing, inks for the electronics industries and trends in inks for metal decorating and plastic container printing.

Streamlining varnish and ink manufacturing processes for maximum economy and efficiency is of increasing importance, so the chapter on ink and varnish manufacture is to be welcomed. Trends in mixing and dispersion equipment are detailed and modern manufacturing techniques including automated and semi-automated plant lay-out are discussed.

A chapter on rheology of printing inks outlines basic principles in an instructive manner. Apparatus for the measurement of viscosity and ink tack properties is described. The relationship of rheological properties with performance of an ink on the press, is discussed.

Testing, control and analysis of inks is given lengthy treatment and there is emphasis on the increasing use of instrumental analytical techniques, with some practical examples.

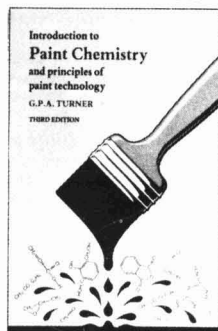
The concluding chapter reviews UK legislation relating to the health and safety and environmental aspects in the manufacture, handling and use of printing inks and raw materials. It deals with handling of chemicals, mechanical and operational aspects of health and safety in ink manufacture and guidance concerning inks for printing food packaging, children's toys etc.

There are a few typographical errors and for one or two raw materials, somewhat conflicting data possibly due to variable information on different

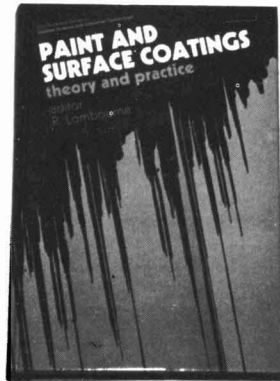
commercial products of the same chemical type. In the opinion of the present reviewer these do not detract from the overall high standard of this book. It should be welcomed throughout the printing ink and allied industries for the wealth of fresh information on all aspects of printing ink technology.

G. H. Hutchinson ■

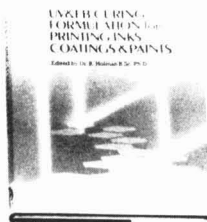
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Paintmakers' Association

A ssiduous readers of this month's *JOCCA* will have noticed that the Paintmakers' crest has appeared on the contents page. This is a result of a decision by both the OCCA and Paintmakers' Councils to nominate *JOCCA* as an official journal of the Paintmakers' Association. This nomination is one further example of the close harmony and good working relationships between the key organisations in the UK surface coating industries and that has already been demonstrated by the joint stand at SURFEX 88 and through participation in the Education and Training Working Party together with the Paint Research Association.

What does the nomination mean for the Association and the Journal? *JOCCA* will feature news of Paintmakers' activities and its member companies will look towards the Journal for important news items, new technology and hopefully, as their preferred advertising medium. The Association is already well served by Paintmakers' member companies, many of whom pay the membership subscriptions of OCCA members in their employment and many managing directors and senior executives of companies are already in membership. What the nomination certainly does not mean is that *JOCCA* will become the voice-piece of the Paintmakers' Association. The nomination will enhance the reputation of the Journal, demonstrates the cohesiveness of the industry and marks a significant achievement for the Association.

Lost Members

The Association has lost contact with some of its members, principally from overseas countries, and is most anxious to re-establish contact with them. If you recognise any of the names below, and know the members' whereabouts, please contact Mrs Raynaud, our Membership Secretary, at Priory House. She will be delighted to put them back on the mailing list:

<u>Name</u>	<u>Country</u>
Akhtar	AS Pakistan
Birch	IM UK
Iyinbo	OO Nigeria
Lad	AR Nigeria
Van der Walt	L South Africa
Whiteside	AE Australia

Chester 89

Readers of Tony Jolly's Chester Conference Column will already be

aware of the excellent technical and social programme that has been organised for the major event of the 1989 OCCA calendar. The majority of Conference papers have now been promised and details of the authors and summaries of their papers will appear in future issues of the Journal. A very attractive registration package will be offered to OCCA members and their partners. Although the venue for the Conference will be the Grosvenor Hotel, Chester, a range of hotels all within easy walking distance of the Grosvenor will be offered to delegates, thus ensuring that all those who wish to participate may do so at reasonable cost.

Whether you wish to register for the whole Conference, attend for one or two days, or only come to the Conference Dinner, Chester 89 is an event not to be missed.

Preliminary Notice

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Chester Conference Column

It is hoped that Simon Lawrence will be able to supply a complete list of papers and authors for publication in November's *JOCCA*. Meanwhile it can be said that, except for a most interesting paper which might still be submitted, the final selection will be made from those already offered.

Unfortunately, Simon is still awaiting a "mug-shot", an extremely minute CV and a short précis of the paper, from some of the authors.

Chris Pacey-Day and I have looked into the financial side of the conference and have discussed the matter with the President and Simon. As a result I will be putting forward a proposal for council acceptance on 12 October regarding the cost to delegates. Hopefully Council will agree with the reasoning behind the proposition and the results of it.

In 1986-87 I contacted hotels of varying grades in Chester and some have even agreed to hold a number of their rooms for you until 1 April. We will be issuing a detailed list of these, with prices, both in the Conference brochure and in

Thames Valley/Bristol Skittles match



Thames Valley-Bristol Skittles: Chris Shaw, Chairman of Bristol presenting the "Walton Trophy" to Richard Stevens (on the right), Chairman of Thames Valley.

JOCCA. Mrs Waterman is presently busy re-contacting the hotels to acquire the final details for this purpose. I trust that everyone will find an establishment to contact and book that will suit their pockets as well as their bodily comforts.

A. C. Jolly ■

BSI Committee vacancies

Council are seeking nominations from members to represent the Association on the following committees: PVC/1/13 Methods of Test for Pigments, PVC/25 Organic Finishes of Aluminium, GME/29/1 Test Sieves: (to represent as required), GME/29/2 Test Sieving and other Sizing Methods (to represent as required), ACE/44 Aircraft Finishes.

Professional Grade

At the meeting of the Professional Grade Committee held on 4 August 1988 the following admissions were made:

Admitted to Associateship:

Archer, Robin Jeremy (*Natal*)

Transferred from Associate to Fellowship:

Gilliam, Brian Frederick (*London*)

Admitted to Fellowship:

Grey, James (*Ontario*)

Thames Valley defeated Bristol Section at their annual Skittles match for the third consecutive year. However, the standard of play of both sides was such that this was more by luck than skill. The event was held at the "Cross Keys", Great Bedwyn.

J. Inshaw ■

Ordinary members

- Airey, B., BSc (*Transvaal*)
- Burd, M. N., BSc (*Cape*)
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