JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION
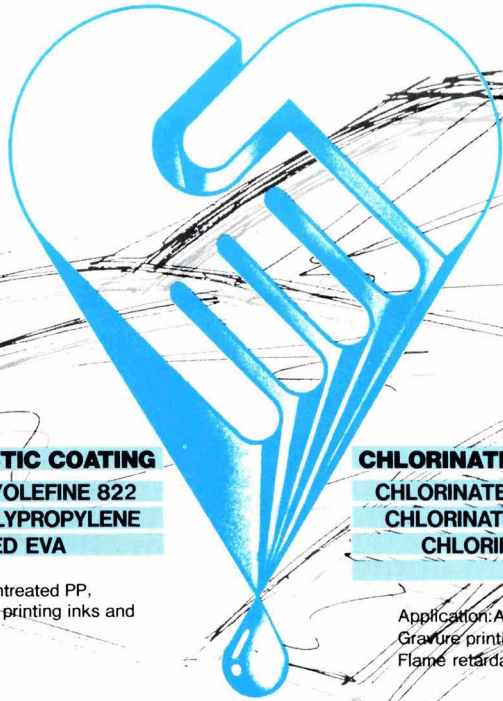
JOCCA

■ Marine & Offshore Coatings

Contents

Cover: Liquid gas carrier 'Gimi', 72480 dwt, managed by Gotass-Larsen, UK, being re-coated in the Hitachi Zosen shipyard, Singapore (Photo by courtesy of International Paint Limited — Part of Courtaulds Coatings).

Forthcoming Features: November — Wood Finishes, December — Waterborne Coatings, January — Corrosion, Process Operation: Dispersing and Mixing. Contributions are welcomed at least five weeks prior to publication date.

Printed by The Herald Press, 17 Rother Street, Stratford-upon-Avon, Warwickshire CV37 6NB   Tel: 0789 66261

From the Honorary Editor

*O*ver the last decade it has been sad to see the shutting down of many well-known established UK surface coating manufacturing companies. It was, therefore, a great pleasure for me to represent OCCA at the Paisley factory of Ciba-Geigy on 21 August and to witness them receiving their Queen's Award for Export and to have the opportunity to tour their £39M investment in new plant for Azo and Phthalocyanine pigments manufacture. The Azo unit is computer controlled and incorporates the latest design, health & safety and environmental concepts.

The feature for this month is Marine & Offshore which is an important part of the UK Surface Coatings Industry due to our involvement in the North Sea Oil & Gas facilities and shipping. Topics covered in this issue include fireproofing of offshore structures, epoxy sealants in seawater service, various aspects of corrosion and anti-fouling coatings.

Another year has flown by since I last announced our Editorial programme and for this year we will see an expansion in this programme. Besides the usual main feature topics and show coverage there will also be special features on specific areas of process operation. The process operation articles will highlight each month the latest developments in a particular area of manufacturing equipment and machinery. The editorial programme for 1990 is as follows:

JOCCA EDITORIAL PROGRAMME FOR 1990

Month	Feature	Process Operation	Show
January	Corrosion	Dispersing & Mixing	
February	Quality Assurance	Computer Controls	SURFEX Preview
March	Adhesion	Filtration	SURFEX Preview
April	Polymers & Resins	Metering Equipment	SURFEX Guide
May	Can Coatings	Storage & Handling	
June	Pigments	Milling & Grinding	
July	Printing Inks	Environmental Control	SURFEX Report
August	1992	IR & UV Curing Systems	
September	Additives & Renewable Resources	Pumping	
October	Physical Testing of Coatings	Energy Conservation	European Paint Show
November	Application & Film Formation	Valves	
December	Weathering (natural and artificial)	Feeding & Packaging	

Contributions are welcomed and should be received by at least five weeks prior to the month of publication. I would be happy to discuss preparation of your article and our recently published 'Guide for Authors' is available on application to Priory House.

Finally, I would like to thank the Honorary Publication Secretaries, Conference Reporters, Works Visitors and Book Reviewers for providing us with excellent contributions throughout the year.

J. R. Taylor ■

From the General Secretary

*1*989 has seen the launch of a new initiative to support the UK and Irish Sections in the promotion of their individual programmes of technical meetings and social functions. A very great deal of hard work, detailed planning and imagination is expended on the development of the programmes which are at the centre of each Section's activities and the committees are always looking for new subject matter to be presented and novel social activities to attract more participants.

Sections are rightly concerned about attendance at some of their meetings, but, given the membership of some Sections, the participation is respectable and compares well with much larger organisations. Sections have developed a variety of methods to attract members and non-members to attend meetings, including individual notification of meetings, posters, notices in the Bulletin and Section diaries. For the 1989/90 season all UK and Irish Sections have been provided with individual 'pocket-sized' programmes produced to a common OCCA format. Two copies of the programme have been sent to each Section member, together with a letter from the Chairman and other information on the Section activities. Ample copies of the programme are available for distribution at meetings and for membership campaigns.

The Section programmes have already attracted great interest and it is understood that another learned society is considering adopting a similar presentation for their activities. It is also likely that the programmes will be offered to overseas Sections for 1990/91.

In addition to the individual programmes, the combined 'Diary of Events' found in the Bulletin has been redesigned as a chronological listing in the form of a poster and is included with this issue of JOCCA. The poster also gives details of Section venues and contacts and it is hoped that it will be displayed on staff notice boards and at technical colleges and perhaps sixth form colleges. Additional copies of the poster will be sent to Sections and are available from Priory House.

I make no apology for the amount of detail on the poster which merely reflects the range of technical and social activities offered by the Association to the surface coating industries. Almost 80 meetings, within an eight month period, ranging from leading edge technology to a liar dice tutorial is no mean achievement! **Support your local Section** and make a commitment to attend at least one technical and social activity during the 1989/90 session.

British Standards Institution

*R*epresentatives are sought on the following Committees:

PVC/1/5 Red Lead Pigments

PVC/21 Surface Preparation of Steel

PVC/25 Organic Finishes for Aluminium

PVC/27/-/3 Zinc Phosphate and MIO Paints

PTC/14 Methods for Determination of Viscosity of Liquids

GME/29/1 Test Sieves

GME/29/2 Test Sieving and other Sizing Methods

Any member wishing to serve on these committees or make a nomination should contact the General Secretary.

Priory House

*V*isitors to Priory House will notice that the offices have now been modernised, re-equipped and repainted internally and externally. The three storey building, of which the Association is the freeholder, has been re-organised and the Association's administrative staff are now situated on the upper two floors, freeing the ground floor for letting to a commercial tenant.

Council is now considering the future development of the site and, in particular, the conversion of the large garage to the rear of the building into additional commercial office accommodation or for use as an Association meeting room. Further ideas under consideration include the upward extension of the garage block and the provision of a library/archive store for the Association's records.

The Association is in the fortunate position of owning its headquarters building without the burden of debt and intends to use some of the surplus funds generated through its exhibitions and publications to invest in the future development of the site. ∎

Ciba-Geigy commissions new pigments plants

Ciba-Geigy Pigments has announced the commissioning of new pigments production and processing plants at its headquarters in Paisley, Renfrewshire, 40 years after pigments production began there. Representing an investment of £39M when fully completed, the new plants include production facilities for azo and phthalocyanine pigments and a pigments grinding unit, using internally developed technology.

The Paisley works has been widely recognised as the most modern pigments factory in the world. The new plant should ensure that it maintains this reputation.

The azo unit, built at a cost of £12M, represents the largest investment of the three new units. Its capacity will in part replace older facilities.

The new grinding unit has its own built-in system for dealing automatically with dust explosions or fires which can occur in this kind of processing. The basis of this system has been developed over the years in the existing grinding unit. It also provides a much cleaner environment for operators through the use of new materials handling techniques.

The phthalocyanine unit introduces a revolutionary new process developed by Ciba-Geigy Pigments for the production of crude blue to the highest environmental standards.

Safety of operation and quality of product were uppermost in the designing of all the new plants. Hazard and operability (HAZOP) studies were carried out on all aspects of the processes to ensure that potential hazards were recognised and removed at the design stage—safety is built-in.

Recognising its responsibility to the environment, and in particular its neighbours in Paisley, Ciba-Geigy has carried out full Environmental Impact studies on the new units.

Designed in close co-operation with HM Industrial Pollution Inspectorate, the new units are ahead of current and anticipated UK and European legislation. Indeed, they are planned to operate to virtually a zero atmospheric emission level.

To ensure quality products all three new units make full use of the very latest technology. Computer control in particular is used throughout. In the azo unit, for example, sophisticated sensors detect minute variations in the process. This information is fed back to the control computer which
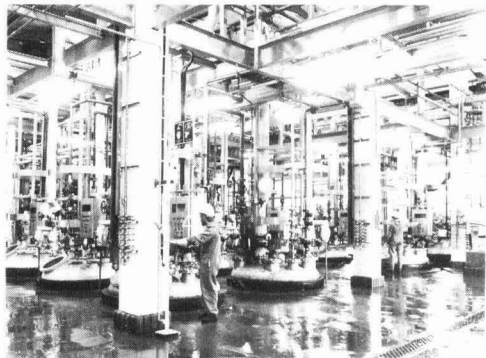
The synthesis floor in Ciba-Geigy's 'Azo V' during commissioning where pigment products are formed in reaction vessels.

Ciba-Geigy Pigments Managing Director Dr Jean-Luc Schwitzguebel (right) receiving the Queen's Award from Major J. D. M. Crichton-Maitland, Renfrewshire's Lord Lieutenant.

automatically makes corrections to the process, ensuring consistent quality combined with improved productivity. The product is, in fact, never touched by the plant operators.

The introduction of stainless steel intermediate bulk containers (IBCs) in all the new plants has dramatically improved handling. These IBCs are, in turn, stored and used through a fully computerised system.

Nearly 800 people are employed at the Paisley works in Research & Development, Manufacturing and Marketing its products to 160 countries.

Research has played a major role in the development of the Division's sales worldwide. More than 25% of its current sales of around £100M come from products developed in the last seven years.

Ciba-Geigy Pigments is this year celebrating its second Queen's Award for Export Achievement, having

increased exports to more than 80% of total production. Its first was received in 1974. The new Award was presented to the Division on 21 August by Major David Crichton-Maitland, the Lord Lieutenant of Renfrewshire. In accepting the Award, Managing Director Dr Jean-Luc Schwitzguebel referred to the company's commitment to continuous improvement and quality at Paisley.

"Quality is the only way we can secure the future of our business: consistent quality of product and quality of service to meet the requirements of our customers, quality of research to maintain a competitive product range, quality of our employees, and quality of our response to the needs of our local community and the environment. This Queen's Award and our recent BS 5750 accreditation show that we are a quality business. Our investment programme will help us remain so".

Rhône-Poulenc buys chemical businesses from GAF and RTZ

*R*hône-Poulenc, the French state controlled chemical group, has purchased RTZ's chemical operation for £568M and GAF's speciality chemical interests for £303M. RTZ Chemicals employs 5,000 people and major product areas include paint thickeners. The business had sales last year of £226M in the UK and £236M to N. America.

Becker's wood division

*T*he wood finishing sector of Becker Industrial Coatings in the UK has changed its corporate identity to bring it into line with its Swedish parent group's timber finishing operation called Acroma. The introduction of Becker-Acroma in the UK will further strengthen the already extensive research and development facilities both here and in Sweden, with particular emphasis on producing environmentally friendly products to meet the new European guidelines.

New EC framework directive on health & safety

*T*he European Community framework directive on health and safety at work, adopted by the Council of Ministers on 12 June 1989, has been published in the Official Journal of the EC. The UK now has until the end of 1992 to bring its health and safety laws into line with the objectives of the directive.

In the coming months, the Health and Safety Commission (HSC) will be considering what proposals should be drawn up to implement the directive in Great Britain. In due course these proposals will be published for consultation before being submitted to Ministers. In view of the wide scope of the directive, it will be necessary to seek a very broad range of views on its implementation.

The directive mirrors the existing Health and Safety at Work etc Act (HSW Act) in setting out broad general duties to ensure health and safety in virtually all places of work. Much of the directive is already covered by existing legislation. However, new regulations will be needed where the directive is more detailed or goes further than present law. The regulations would be intended to maintain the existing system of UK health and safety law by building on the general principles of the HSW Act and in the main would be designed to make explicit what is implicit in existing law.

(See Tony Hinton's article on p415).

Tankfreight-Vinamul

*T*ankfreight, the UK's largest third party bulk distributor, has won a £3 million contract to move chemicals for the Unilever company, Vinamul, which produces polymer emulsions for the adhesives building, paint and allied industries.

European coated steel standards

*P*eter Munn, one of OCCA's representatives on BSI committees, reports on a new European standard: 'The European Committee for Iron and Steel Standardisation is establishing a new Working Group for the preparation of European Standards on automatically blast-cleaned and coated steel products,' and the inaugural meeting of the Group will take place shortly. International Standards (ISO 8502) and several national Standards already exist in this area.

'It is not clear at the moment through which organisation the interests (if any) of the UK will be represented. Since the work may be parallel to work currently under way in the European Committee for Standardisation CEN/TC 139, on which the BSI looks after UK interests, they have been asked to contact their Committees for a nominee to participate in the Working Group as a paint expert.'

Products

Crown offshore coatings

*C*rown Protective Coatings have developed Ferox moisture-cured urethanes for offshore steel protection. They can be applied to surfaces as low as freezing point, and will cure as low as $-9°C$ with a coating thickness of only 150 microns needed for application. On platforms Ferox Pure Urethane Coal Tar Pitch Composition, a high build coating, is ideal for splash zone protection. It sets quickly giving early resistance to corrosion and can be applied in very thick coatings. Other platform surfaces are coated with a primer, an intermediate and a top coat. Micaceous Iron Oxide paint provides a build coat for use on undercoat. This has a high resistance to water and chemical attack. The top coat is of Ferox Pure Urethane Gloss, a high gloss retention paint with excellent resistance to UV discoloration, abrasives and chemicals.

For further information Enter J199

New UCAR oil industry coatings

*U*nion Carbide have introduced advanced new thermally sprayed coatings (often designated 'overlays'), designed specifically for the oil industry. These have been developed to reduce wear and corrosion problems in sub-sea and surface equipment used in offshore oil production. LW-26 is from the UCAR coatings family of fused high density materials with typical applications for gates and seats in valve assemblies.

LW-45 is a tungsten carbide/cobalt/chromium material introduced to protect components in a wider operating range. This is ideal for critical valve components and other high pressure applications. UCAR LW-2, based on tungsten carbide and cobalt, can be applied to 0.045″ thickness and can be used to repair worn components, without requiring a separate salvage undercoat.

For further information Enter J200

Equipment

Computer controlled dispensing

Douglas Instruments has released a new addition to its range of Liquid Handling modules which can be easily adapted using an IBM-compatible computer to any automatic dispensing protocol. This is a compact high-resolution syringe driver for almost any disposable or gas-tight syringe. The system includes stepper-motor driven pumps, valves and syringes, and can be expanded to any number of modules. For example, several syringes or pumps can be loaded with paint components and mixtures can be dispensed on demand, or using the user's own software.
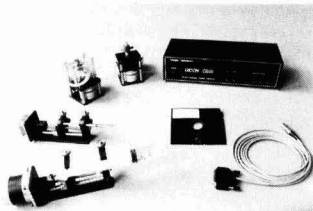
For further information Enter J201

Baxi's timely Volcoater

A major move towards Just-in-Time production has been made possible by major heating appliance manufacturer Baxi of Preston, following the installation of its third Volstatic Volcoater powder coating plant.

The latest equipment installed by Baxi consists of a Volstatic Volcoater with two Waggler units, one unit carrying five of the new Volstatic HP1000 automatic powder guns and the other unit carrying three guns. Also included in the contract is an eight-gun generator console, fluid bed and ventures, and a Solidspray 90 'XC' manual powder coating unit.

Extraction from this booth is directly to a reverse pulse cartridge filter incorporating a fluidised base from which recovered powder is automatically drawn, sieved and returned to the fluid bed. The cartridge and collector module is dedicated to one colour and can be easily removed and replaced with another.

The complete system is mounted on a platform to allow fast and efficient removal from the line so that colour change clean down can be carried out without loss of production.

For further information Enter J202

New limpet case taper

A new fully automatic uniform size case taper, Model XL33 from Limpet Tapes Ltd, co-ordinates top flaps closing with top and bottom flaps sealing for on-line packaging operations. Handling uniform runs at a rate generally up to 20 cases per minute, the XL33 accommodates units up to a maximum of 500mm wide x 500mm high x 650mm long. The XL33 can be free standing or mounted on casters for mobility about the packing areas. The casters feature a 'clip-down' safety brake that, once engaged, ensures no extraneous movement during operation.
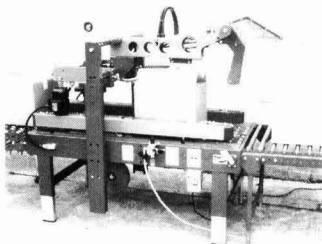
For further information Enter J203

3M establishes RPE helpline

Intended to help users, specifiers and other suppliers, the respiratory protective equipment (RPE) Helpline service from 3M Occupational Health and Environmental Safety has been specifically designed to assist with queries relating to the new UK Regulations as well as the proposed European directives. The helpline number is 0344 58546.

Literature

Latices in Europe

Van Gogh might have stuck to his oils, but he'd be increasingly alone in Europe today: environmental concerns over paints and adhesives will create a $1.48 billion (B) European market in vinyl and acrylic latices by 1993, says a new 306-p study, at the expense of solvent-based products such as oil paints.

This is the prediction of "Vinyl and Acrylic Latices in Europe" (#E1077), a report published by Frost and Sullivan Ltd, which analyzes what's happening at present with projections to 1993. The 1993 dollar volume will represent growth over a 1988 base of $1.17B, using constant 1988 dollars. In tonnage terms, more than 1.12M metric tons of latices used in 1988 in Europe will pile up to 1.24M metric tons by 1993.

"Over the next five years it is expected that specialized emulsion paints for use on wood, now small in volume, will gain in market share as the advantages of water-borne paints over solvent-thinned products become more appreciated. Pure acrylic latices in particular will benefit from this trend." Accounting for 431,000 metric tons of latices used in 1988, or 37% of the entire market consumption, paints comprise the largest applications area. The study predicts some 484,000 metric tons will go here by 1993.

Uses in adhesives amounted to 317,000 metric tons in 1988, constituting the market's second largest sector, 28% of its total; the expectation is that by 1993, 357,000 metric tons will be bound up here.

Nationally, W. Germany's high paint offtake and particularly strong adhesives industry made it the largest individual market, $383M, or almost DM663M in 1988, or 325,000 metric tons of latices. There is a "vigorous DIY market for emulsion paints and substantial latex consumption" in the UK, the second-largest consumer, $220M was spent here in 1988, or £121M for 197,000 metric tons of latices. France has a notable capacity in producing latex raw materials, including Europe's largest vinyl monomer plant. The 1988 consumption of latices there ran $143 M, or Fr834M, spent toward 146,000 metric tons of product.

The report details the recent competitive position of suppliers as well, showing BASF and Hoechst to be overall largest in the field.
The price of report #E1077 is $3,550.
For further information Enter J204

The New Generation

The versatile BENTONE SD series of rheological additives is outstandingly easy to use. Pregelling and polar activators are no longer necessary – simply incorporate them directly into the millbase. You can thus increase manufacturing flexibility and reduce labour and raw material costs. **Simplicity itself...**

For more information on the BENTONE SD series contact

STEETLEY MINERALS LTD.
P.O. Box 2, Retford Road, Worksop, Notts. S81 8AF U.K., Tel. (0909) 475511, Telex 547901

NL CHEMICALS EUROPE, INC.
rue de l'Hôpital 31, B-1000 Brussels, Tel. (02) 5120048, Telex 24662

NL Chemicals

News

Strong worldwide chemical merger and acquisition activity

*T*he scores have been tallied and the results are in (see tables below) The number of mergers and acquisitions in the chemical and allied industries hit nearly 1,300 in 1988, up 11% from 1987. Eastman Kodak topped the list of big deals with its US$5.1 billion take-over of Sterling Drug. And three European firms—Elf Aquitaine, ICI and Rhone Poulenc—were tied for the distinction of most transactions completed: each wrapped up 13 deals last year, according to Kline & Company, an international business consulting firm based in Fairfield, NJ.

Kline have just released their comprehensive report, Chemtrak, which covers 1988 chemical mergers/acquisitions and is available upon subscription.

Transactions in chemicals and allied products by region 1988

Region/country	Number of transactions	% of total
United States	723	56%
Western Europe	404	31
Japan	24	2
Other	132	10
Total	1,283	100%−a

a — does not add due to rounding

Most active acquirers worldwide 1988

Company	Headquarters	Number of acquisitions
Elf Aquitaine	France	13
ICI	UK	13
Rhone-Poulenc	France	13
Laporte Industries	UK	11
Akzo	Netherlands	11
Cookson Group	UK	10

Acquisitions and mergers in chemicals and allied products by type of business 1988

Category	Number of transactions	% of total
Speciality chemicals	217	17%
Pharmaceuticals and health care	211	16
Fabricated plastics and rubber	148	12
Tonnage chemicals	136	11
Consumer products	80	6
Other	491	38
Total	1,283	100%

For further information Enter J205

Meetings

Analytical Chemistry

*O*pen learning courses in Analytical Chemistry from October 1989 to January 1990 with Workshop 3-5 January, Thames Polytechnic. For further information contact: L. A. Hart, RSC, Burlington House, London W1V 0BN, UK.

SSPC '89

*T*he Steel Structures Painting Council will hold its National Conference and Exhibition "Protective Coatings for Industrial Structures" at the George R. Brown Convention Center in Houston, USA, from 3-8 December 1989. For more information contact Rose Mary Surgent on USA-412 268-3326.

FSCT's 54th Paint Show

*L*arry Speakes, formerly Chief Spokesman for the Reagan Administration, will present the Keynote Address at its Opening Session on 8 November, in the Grand Ballroom of the New Orleans Marriott Hotel. The topic of his address will be "A Look at the Bush White House." The Annual Luncheon Speaker on 10 November will be the distinguished writer, George Plimpton. The Federation's 67th Annual Meeting and 54th Paint Industries' Show will be held on 8-10 November 1989 in New Orleans, LA.

The Paint Show, with over 220 exhibitors from the US, Canada and Europe, will be held at both the New Orleans Hilton's Exhibition Hall and the adjacent Rivergate Exhibition Center.

The theme of the Federation's annual Meeting is " Coatings Worldwide: Meeting the Needs of the Nineties." Program Chairman George R. Pilcher, Hanna Chemical Coatings, and his committee are developing a schedule of presentations which will focus on timely issues including: Corrosion Seminar — "New Approaches to Corrosion Evaluation"; Professional Development Committee Seminar on "Advanced Topics in Coatings Research"; Session on " Use of Computers in the Nineties"; Manufacturing Committee Seminar on "Manufacturing for Quality and Profitability"; Symposium on "Regulation in the Nineties"; Symposium on "Raw Materials in the Nineties"; Roon Award Competition Papers; Constituent Society papers and Papers presented on behalf of affiliated overseas coatings organizations. Culminating the Annual Meeting programming will be the Mattiello Lecture, "Learning to Leap: Rising to the Technical Challenge of Today's Coatings Industry," to be given by Dr Marco Wismer, formerly Vice President, Science and Technology, PPG Industries, Inc. For further information contact: FSCT, 1315 Walnut Street, Philadelphia, PA 19107, USA, or Tel: USA-215/545-1506-1507. ∎

A new approach to the development and testing of antifouling paints

by C. T. Bowmer and G. Ferrari, TNO, Laboratory for Applied Marine Research, Post Box 57, 1780AB, Den Helder, The Netherlands

A growing problem which currently faces the manufacturers of antifouling paints is how to maintain a high standard of performance for coatings used on ships and offshore structures, under increasingly stringent regulations for the protection of the marine environment.

The problem of fouling

Fouling and corrosion are the two most important problems in the protection of ship hulls and other metallic constructions at sea. This article is concerned with fouling, and attempts to weigh up the economic necessity of its prevention against the potential damage (also economic) to the marine environment. The second aspect of marine corrosion is not considered here.

The term fouling implies the growth of plants and animals which settle as spores and larvae on submerged surfaces, and attach themselves, sometimes very firmly, as in the case of barnacles (see Figure 1). The speed of settlement, the species settling and their subsequent growth vary geographically

Figure 1
Fouled coating.

Fouling is generally faster in the tropics with warmer temperatures. However, even in cold north European waters, a luxuriant growth of plant and animals can appear with alarming speed. The consequences are that the frictional resistance of ships is greatly increased, affecting cruising speeds and fuel bills. The corrosion of surfaces is accelerated, as the fouling organisms increasingly damage the protective coating. Navigation buoys and offshore constructions increase in weight, so affecting their buoyancy. The catalogue of problems created by fouling has a long history and the economic costs are large.

In general, fouling is combatted by means of antifouling (AF) paints containing one or more toxic compounds. These toxic compounds are present at the paint-water interface and kill off the settling organisms, so preventing fouling at the initial build-up stage. Thus, for an effective prevention of fouling, a definite and constant threshold concentration of the toxic compound is desirable at the paint surface; the so-called lethal concentration. The release rate of the toxic compound from the matrix in which it is incorporated has to remain high enough for long periods (preferably years). Antifouling paints may be classified into three basic categories.

1. Conventional AF paints

The binder or matrix in these older types of paints is usually rosin. This natural product is soluble in seawater, and in this way, the toxicants (biocides) initially dissolved in the paint became available at the coating surface. The biocides used in these paints are (or were) lead, arsenic, mercury and copper, as oxides.

However, with a rosin matrix, only thin and structurally weak films are possible. Furthermore, the leaching rate of the toxicant(s) is very high. The net result is that the concentration drops quickly below the lethal level necessary for the prevention of fouling. The working life of such paints is relatively short, between 6 and 12 months.

2. Long-life AF paints

The binder of these paints is insoluble in seawater and the toxicants have to diffuse to the paint surface through the polymer matrix. The main binders employed in these paints are: vinyl and acrylic resins and chlorinated rubber, while the main toxicants used are cuprous oxide and organotin compounds. Although the release of the toxicant occurs through channels in the paint, caused by the dissolution of the biocide and other substances contained in the layers nearer to the paint surface, diffusion of the toxicants along concentration gradients is the main driving force. It is understandable that the leaching rate decreases with increasing distance to the paint surface and that after a given period of use, the diffusion distance becomes too large. Despite high quantities of remaining toxicant in the paint, the concentration at the surface eventually falls below the necessary lethal levels. With these paints, it is possible to realise an effective protective lifetime of between 18 and 24 months, after which the coating must be removed and completely replaced.

3. Self-polishing copolymer AF paints (SPC's)

In these paints the biocide, in most cases tributyltinoxide, is chemically bound to the acrylic polymer. On contact with seawater it is released by hydrolytic processes occurring at the paint surface; release rates are no longer dependent on diffusion. Release occurs in a controlled and constant manner, depending on water movement along the coated surface. After release of the toxicant, the empty matrix of the polymer is effectively washed away, e.g. when a ship is sailing, or by tidal currents around fixed structures, exposing a fresh layer of coating. Besides tributyltinoxide (TBTo) the paints may also contain tributyltinfluoride (TPTF, TPTIC1). Furthermore, they may contain substantial amounts of cuprous oxide. SPC's possess a broad spectrum activity against a large range of fouling organisms.

The consistent performance of SPC's during the lifetime of a coating and the knowledge that its durability is predictable and proportional to the film thickness, are great advantages in comparison with other systems. The average working life of an SPC coating is roughly 4 to 5 years. Other secondary advantages are the hydraulic smoothing effect on the paint's

Q Does your epoxy system provide you with –

Enhanced adhesion, particularly to difficult substrates such as aluminium, rusty and oily steel?

Improved water and corrosion resistance?

Flexibility and impact resistance?

Chemical resistance to a wide variety of fluids?

If you can answer yes to these questions then you do not need to use ELP3 the new odour free epoxy modifier from Thiokol Chemicals, Morton Thiokol Limited.

For further information, contact us.

THIOKOL CHEMICALS

Division of Morton Thiokol Limited

University of Warwick Science Park,
Sir William Lyons Road,
Coventry CV4 7EZ
Telephone: 0203 416632
Telex: 311412 THICOV G
Fax: 0203 414745

A subsidiary of Morton Thiokol Inc.

surface texture, and the possibility of repainting old surfaces, even those coated with a long-life AF system, without having to remove the old coating first.

The consequent increase in the time between dry-docking intervals, coupled with reductions in the length of stay in dry dock, as well as reduced friction when sailing (due to the effective prevention of macrofouling) make these paints economically attractive. From a technical point of view, SPC's have been developed into very satisfactory products with a high level of performance and cost saving.

All that said, however, the original assumption that organotin when dissolved in seawater would quickly degrade to harmless by-products, has proven to be far too optimistic. Degradation in the environment does indeed proceed relatively quickly but the by-products are not harmless and organotins are toxic at levels which were previously unheard of.

Organotins in the marine environment, are the rumours and accusations true?

In a word, yes. In the early 1980s, organotin was implicated in failures of shellfish crops occurring in north western France. The finger was pointed at a link between the intensity of pleasure boating activity and maricultural problems. There were spawning failures, growth was poor and strange shell deformities were noticed in adult oysters. These problems were found to be increasingly widespread, affecting expensive commercial species such as scallops and oysters, as well as mussels. Not surprisingly, salmon and trout farms, where OT products had been used to give antifouling protection to cage and net systems, reported failures also. By 1986, there was enough evidence to prove all these problems, at a multitude of locations in the US and Europe.

One of the most bizarre effects of organotin occurred in the dogwhelk, a small shore-dwelling 'sea shell', where the females became reproductively sterile due to the growth of an unwanted penis which blocked the oviducts. This fact raised a few eyebrows and a few smiles, but did it mean anything in the world of policy making? It was shown that dogwhelks around the entire UK coast were locally sterile, and nearly always in the vicinity of harbours[1]. Later, it was established experimentally, both in the laboratory and in the field, that this was as a result of organotin[2] compounds in seawater. The most significant factor is that this small organism is a predator on the shoreline and apparently controls much of the local diversity of marine life on rocky coasts in north western Europe.

The dogwhelk was, and still is, in danger of disappearing in many areas. Similar species in the US were shown at around the same time to be affected in a like manner. The condition, rather colourfully called imposex is irreversible, and there were fears that large scale changes could occur along the shoreline, in itself an important amenity and resource.

It is now known that tributyl tin, closely followed by related organotin compounds, restrict the growth of clam larvae[3] at concentrations of ca. 10ng.l^{-1} or 1:1x10^{11}. Even by toxicological standards, such levels are extremely low. For example, copper has a 96 hour LC$_{50}$ (lethal concentration) to many marine invertebrate organisms of roughly 1mg.l^{-1} or 1:1x10^6. Imposex in dogwhelks can be caused at concentrations of as little as 1ng.l^{-1} (1:1x10^{12}). Equally alarming was the fact that pathological effects could be induced at such low levels, i.e. imposex and shell deformation in oysters, clams and mussels. It may be concluded that organotins are not only extremely toxic, but cause harmful side-effects to a wide variety of non-target species, including *both* ecologically and commercially important organisms.

If it had not been for a direct economic conflict between two large users of the marine environment, i.e. a fast-growing maricultural industry and the shipping and pleasure craft industries, then we suspect that few would have listened to the biologists and little action would have been taken.

The net result of this conflict is an unhappy compromise: organotins have been banned for use on pleasure craft, fish cages, fishing trawlers and small floating structures in many countries (although regulations vary), with the aim of removing a very real threat to inshore waters. Many biologists would like to see a total ban on the production of organotins for use in the marine environment.

As far as the paint industry is concerned, a portion of the SPC market has already disappeared and the threat of further restrictions relating to the production of OT's does not appear to be over yet, e.g. a maximum tolerable leaching rate is expected to be introduced in the US. Japan is expected to introduce similar rules this year, and the OECD will be issuing guidelines for OT containing paints which are expected to be adopted by many European countries. In general, organotin based antifouling paints are still permitted for commercial shipping, but the future remains uncertain.

Solutions for the future

At the moment, there is no proven alternative to organotin containing SPC coatings. From an economic standpoint they are still necessary and, for reasons already explained, long-life AF paints are no substitute. Besides, many long-life paints contain OT's anyway. The production of a non-toxic AF system seems a long way off; some experts think as far away as 15 to 20 years[4]. This is the ultimate answer to escape from the problem, and a continuing research effort in this direction is of great importance.

But the most immediate question that needs to be asked is what can we do to reduce organotin usage as quickly as possible in the short to medium term.

In our opinion, a limited number of options seem to be open.

1. A logical step and an apparently attractive one is to take a new look at copper based AF paints, and to include this toxicant, whose properties are well known, in an SPC 'type' coating. While no toxicants are desirable in the marine environment, copper is generally accepted as being infinitely preferable to organotins.

2. There is clearly a move underway on the part of paint and raw materials manufacturers to examine other (organic) toxicants, as possible substitutes for organotins: here, the stumbling block will be their degradability and again the question of environmental effects arises. It will have to be made certain, that new chemicals used in AF paints do not cause lasting effects among non-target marine organisms. Some of this type of paint system are already on the market, promising relatively long-term antifouling protection. Many options are available among modern agricultural biocides and so-called 'designer' toxic chemicals and consequently, there is always the possibility of repeating the mistakes associated with organotins.

3. The third possibility applies to new paints in general, as well as to existing OT containing coatings and indeed heavy metal based products. The release of the toxicant must be enough to provide adequate antifouling protection, but it need not be, as was frequently the case, present in such quantities that waste (non effective) toxicant is released to the environment in large quantities. A look at the paint manufacturers' brochures quickly confirms that many now claim to produce this type of paint using tributyl-tins.

The Organotin story is far from being over. One of the knock-on effects already being felt is that far stricter testing (on environmental grounds) is being demanded by many regulatory authorities for new antifouling products than was previously the case. Moves to restrict paints on the basis of maximum allowable release rates are designed to prevent the wasteful and unnecessary use of toxicants. This again comes back to problems of testing, only this time to the efficiency of the paint itself.

Antifouling paint testing at TNO Den Helder

The TNO Laboratory for Applied Marine Research has played an important role in the development and testing of various antifouling systems over the last 25 years and has the experience and necessary test facilities to evaluate products along the lines stated above. The laboratory in Den Helder houses two research groups: the paint and corrosion research group of CPM-TNO and the field ecology group of MT-TNO (Biology Department); both have long experience and apply the most up-to-date methodologies in their respective fields.

Through a pooling of information and ideas, combined with a large variety of test systems (both in the paint field and in the area of environmental research), the Den Helder laboratory can now offer an integrated approach to paint research, suited to the changing climate of economic and environmental awareness.

1. Facilities for testing coating performance

□ Test Raft (Figure 2): This is used to test the growth of fouling communities on antifouling treated test panels. To achieve this, the panels are mounted in racks and exposed at the desired depth in the sea, at a sheltered location known for its fast rate of fouling growth. A useful procedure is to expose test panels in the growing season until a reference panel with a paint coating but no toxicants is 100% overgrown.

Figure 2
Test raft with lifting beam, in Den Helder harbour, for testing the antifouling properties of paints exposed on submerged test panels.
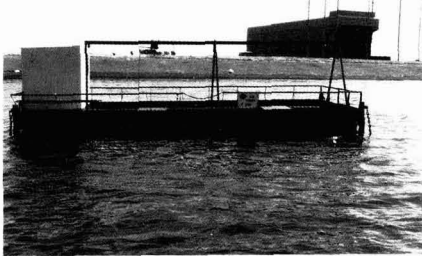
□ Rotor Apparatus (Figure 3): This consists of a cylindrical drum with a diameter of 80cm, placed in a container with 500 litres of natural seawater. Curved, antifouling-treated, test panels are attached to the outside of the drum, and the erosion rate of the coating is measured. The drum is rapidly rotated and its circumferential speed is usually equivalent to 17 knots, but can be varied between 10 and 20 knots. Throughout the test, the paint thickness is measured with a micrometer at regular intervals (14 days), always on the same 10 places on a test panel. Knowing the decrease in paint thickness as a function of time, the erosion rate is calculated. To perform these measurements accurately, a special

Figure 3
Rotor Apparatus, showing the revolving drum with attached painted test panels lifted out of the seawater vat. The rotor apparatus is used to test the rate of erosion of an AF coating at a standard 17Kt.
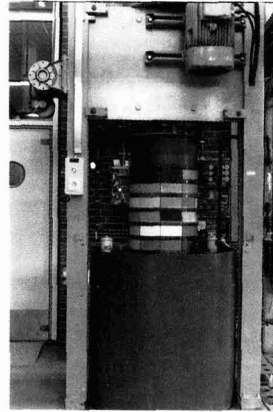
apparatus has been developed, with which it is possible to repeat thickness measurements at exactly the same locations. Registration and analysis of measuring data is done by a computer. On each drum, up to 70 panels *(8x12cm) can be mounted, so that this test is ideally suited to the development of the optimal paint formulation. The "rotortest" in combination with exposure on the raft are essential for assessing the eroding properties and the antifouling performance of paints.

□ The Rotating Disc Test: The advantage of a rotating disc is that the flow rate of the seawater is a function of the radius of the disc.

In this way it is possible to establish the relationship between the erosion rate and the flow rate (simulated ships speed), using antifouling painted test discs with a diameter of up to 80cm. Furthermore, it is possible to apply cathodic protection and to study the behaviour of a complete paint system. By alternating the rotation exposures with exposure on the raft, one can stimulate a ship which is sailing for some time and then lies still in the harbour for a definite period. Figure 4 illustrates this test system.

Figure 4
Rotating disc apparatus. The photo shows a series of tanks with hydraulic and electric motor driven arms for rotating up to 80cm diameter antifouling painted discs. The thickness of the coating at fixed distances from the centre is measured periodically to indicate the relationship between speed of waterflow and the erosion rate of the paint.
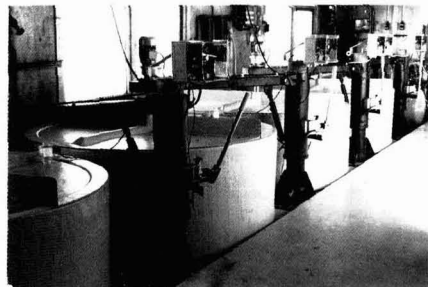
☐ The ASTM standard method for testing organotin release rates from antifouling coatings.

With this method, which is still under development at TNO, the rate at which organotin is released from an antifouling coating is measured. This is done by measuring the content of organotin in the seawater using graphite furnace atomic absorption spectrophotometry (GF-AAS), after a specified period of exposure to panels in a small rotor system. With this test method it is possible to measure changes in solvent extractable, tributyltin release rates. Quantitative measurements of the release rate are necessary to help in the selection of materials, to provide quality assurance and to understand the performance mechanism. TNO Den Helder has the facilities and is at present gaining experience in the accurate performance of this ASTM test. Figure 5 shows the test apparatus.

Figure 5

Test apparatus for measuring the release rate with time of the major toxicants (organotin) from antifouling coatings. The polycarbonate cylinders, treated with an antifouling coating, are rotated in a vat of standard seawater, and the concentration of the biocide released is measured periodically as $\mu g.cm^{-2}.d^{-1}$.
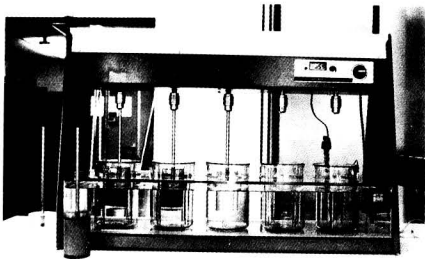
With these tests, a balance can be struck between the initial choice of toxicant and the paint formulation, the right level of toxicant release necessary to prevent fouling, but which avoids excess toxicants entering the environment. Furthermore, the ASTM test is now required by the EPA to licence paints in the USA.

2. Environmental testing of antifouling paints and toxicants

The field ecology group operates a variety of model ecosystems, ranging in size from $1m^3$ (6 units, see Figure 6) and $2.2m^3$ (12 seawater and 14 freshwater units) to large concrete basins of $22.5m^3$ (8 units) capacity. Model ecosystems or mesocosms are small-scale living replicas of the environment at large, in which many biological processes (including ecotoxicological effects) can be studied under controlled conditions. In these systems, contaminated harbour sediments, flyashes, oil spills, organic environment and also pure toxicants can be examined for their ecotoxicological effects on marine ecosystems.

Generally, each unit or basin contains a 15 to 30cm deep layer of sediment, which is overlain by some 15 to 45cm of seawater. Depending on the type of environment to be modelled, a series of test animals and plants are chosen, introduced in the basins and allowed to acclimatize to the system. The seawater is continually replaced at a controlled rate, and parameters such as temperature, salinity and water flow are continually registered.

This facility is being expanded to automatically record O_2, pH, the delivery of toxicants, etc. incorporating an alarm function to warn of system failure, or to warn when set parameter thresholds are exceeded.

With model ecosystems it is possible to control the

Figure 6

Two of MT-TNO's five model ecosystems are shown on the outer harbour dike at Den Helder, comprising $6 \times 1m^3$ elongate tanks and 8 to $12 \times 2.2m^3$ circular tanks for larger experiments.

environmental conditions to a greater or lesser degree: with strictly controlled conditions the systems can be used for standard bioassay tests, or when allowed to function more freely, a greater degree of complexity can be achieved, allowing the systems to function in a similar manner to the field situation. The introduced test organisms form the focus for effect studies. However, the development of phyto and zooplankton communities in the water column can also be followed, as can the development of other 'incidental' organisms, e.g. animals introduced with the sediments, or entering the systems as larvae.

An advantage of this type of mesocosm investigation is that effects can be evaluated at different levels of complexity, i.e. among individuals, populations, or at the more complex ecosystem level.

Processes such as bioaccumulation of toxicants in the tissues of the test organisms are followed, and compared to the biodegradation in abiotic compartments, e.g. sediment etc. A balance is made up for the overall fate of contaminants in the model ecosystems.

The ability of a toxicant to disturb the organisms functioning (at the level of the individual and the population) can be evaluated in a number of ways, depending on the length of the test. The following parameters are routinely measured:
▷ mortality,
▷ growth,
▷ alterations in external morphology (deformations),
▷ reproduction;
    egg production,
    larval survival,
▷ population dynamics,
▷ pathology,
▷ parasitology.

In practice, the methodology used and the parameters chosen depend on the test animals involved and can vary considerably.

For the testing of antifouling paints, small painted panels (15x7cm) are loaded into a dosing apparatus, and the system water supply is led through this device and then released continuously into the model ecosystem units. Usually, between three and five concentrations are used alongside a clean control tank. Where possible, a contaminated reference, for example a copper dosed unit, is included, and can be of great assistance in the interpretation of data.

Figure 7

Small scale (1m³) model ecosystem tanks filled with a 15 to 20cm layer of marine sediment, covered with a 30cm deep water-column. The test animals are allowed to burrow freely into the sediment, or are hung in baskets in the water-column. The supply water is pumped through a dosing apparatus consisting of AF coated test panels, which delivers a constant concentration of the biocide to the model ecosystems.
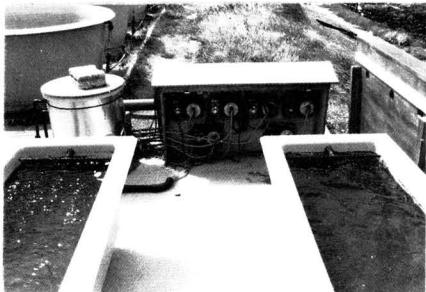
In recent years, devices for dosing antifouling toxicants from the above mentioned painted panels direct to the test ecosystems have been developed and refined at TNO. These dosing devices are controlled by the seawater flow and can stimulate ships speeds of up to 17kts, i.e. realtime release rates in the marine environment. In this manner, not only the toxicant can be tested for undesirable side-effects, but the formulation and manner of release are also examined.

Conclusions

In current and future projects we are combining research into optimal paint formulation and antifouling performance with information on environmental fate, for existing and new products. Our aim is to evaluate the technical performance of a new product and to give *early warning* of potentially damaging side effects to the marine environment in the *R&D phase*, before large-scale resources are committed to its production. It is our considered opinion that investment in adequate testing of a product will far outweigh the potential loss of an already marketed product being banned or restricted on environmental grounds. The encouragement of a responsible attitude to product testing may prevent the occurrence of similar detrimental environmental effects to that created by organotin over the past decade.

References

1. Bryan, G. W., Gibbs, P. E., Hummerstone, L. G., and Burt, G. R.' The decline of the gastropod *Nucella lapillius* around south-west England: evidence for the effect of tributyltin from antifouling paints', *J Mar. Biol. Ass. UK*, 1986, **66**, 611.
2. Bryan, G. W., Gibbs, P. E., Burt, G. R., and Hummerstone, L. G. 'The effects of tributyltin (TBT) accumulation on adult dogwhelks, *Nucella lapillius*: long-term field and laboratory experiments', *J. Mar Biol. Ass. UK*, 1987, **67**, 525.
3. Laughlin, R. B. Jr, Gustafson, R., and Pendoley, P., 'Chronic embryo-larval toxicity of tributyltin (TBT) to the hard shell clam *Merenaria mercenaria*', *Mar. Ecol. Prog. Ser.*, 1988, **48**, 29.
4. Furtado, S. E. J., 'The prospect for non-toxic antifoulings', in: Symposium; antifouling, how to proceed? Schevening, The Netherlands, 17 Sept. 1987. TNO Paint Research Institute report, V-88-058, 30pp. ∎

Conclusions

In this research the corrosion of steel under a thin varnish film is quantified. The corrosion process is forced by exposing the steel/varnish system to atmospheres contaminated with SO_2 and NaCl.

The high permeation rate of SO_2 through the varnish film induces the formation of ferrous sulphate at the interface, corrosion of the underlying steel, and subsequent blistering of the coating. The corrosion of steel is directly proportional to the concentration of SO_2 in the atmosphere.

On the contrary, the low ionic permeability of the varnish film hinders the underfilm corrosion of the steel by chlorides in atmospheres containing NaCl; the steel does not show any appreciable sign of corrosion after 500 hours of exposure.

In alternate exposures to atmospheres polluted with SO_2 and NaCl respectively, the NaCl inhibits to a certain extent the metallic corrosion, since the corrosion rate decreases as the NaCl content in the atmosphere increases.

Acknowledgements

References

1. Feliu, S. and Morcillo, M., "Corrosión y protección de los Metales en la atmósfera", Ed. Bellaterra, Barcelona, 1982.
2. Igetoft, L., *Ind. Eng. chem. Prod. Res. Dev.*, 1985, **24**, 375.
3. Morcillo, M. et al., *JOCCA* (submitted for publication).
4. Funke, W. et al., Proc. XV Fatipec Congr., Amsterdam, 1980, 111-287.
5. Bechtle, S., Master's dissertation. II. Institut für Technische Chemie der Universität Stuttgart, 1985.
6. Funke, W., Proc. Int. Conf. Surface '66, Basel, 1966, 237.
7. Funke, W., *Farbe und Lack*, 1987, **84**, 493.
8. Haagen, H. and Funke, W., *JOCCA*, 1975, **58**, 359.
9. Feliu, S., Galván, J. C. and Morcillo, M., *"Progress in Organic coatings"*, 1989, **17**, 143.
10. Dickie, R. A. and Floyd, F. L., 'Polymeric materials for corrosion control". ACS Symp. Series 322. Washington, 1986, 1.
11. Funke, W. et al., *JCT*, 1986, **58**, 79.
12. Hernández, L. A., Ph Doctoral Thesis. ETSI Minas. Universidad Politécnica de Madrid, 1988.
13. Funke, W., Haagen, H., Krieg, E. and Zeh. J., Proc. XVII Fatipec. Congr, Lugano, 1984, IV-177.
14. Zankel, K. and Ahearn. J., "Material damage from acid deposition. Phase I: Planning study (report)". Electric Power Research Institute, Palo alto (California), 1987.
15. Svoboda, M., Kuchynka, d. and Knapek, B., *Farbe and Lack*, 1971, **77**, 11.
16. Svoboda, M., Klícova, H. and Knapek, B., *JOCCA*, 1969, **52**, 677.
17. Funke, W., *JOCCA*, 1979, **62**, 63.
18. Glass, A. L. and Smith, J., *J. Paint-Tech.*, 1967, **39**, 490.
19. Corti, H., Fernández-Prini, R. and Gómez, D., *"Progress in Organic Coatings"*, 1982, **10**, 5.
20. Ambler, H. R. and Bain, A. J., *J. Appl. chem.*, 1955, **5**, 437. ∎

Performance of some commercial epoxy-based coatings for use as sealants in seawater service

by J. A. Carew, J. K. Cheriyan and A. M. Hadi, Materials Application Department, Division of Petroleum and Petrochemicals, Kuwait Institute For Scientific Research, Kuwait

Abstract

The suitability of some commercial epoxy-based coatings as sealants for welded carbon steel piping joints under hydrodynamic seawater conditions were investigated.

The effects on the sealants' adhesive shear strengths at different curing temperatures and humidity levels during the curing stage were determined. The ageing characteristics of the sealants under ultraviolet irradiation were studied. The erosion resistance and adhesive properties of the sealants were investigated using a rotating disk apparatus.

The results show that surface preparation had an effect on the overall performance of the sealants. The adhesive shear strengths of the sealants improved with an increase in curing temperature. The erosion resistance of the sealants appeared to have some correlation with their adhesive shear strength.

Introduction

Cement-lined carbon steel pipes are commonly used in the petroleum and petrochemical industries for seawater piping systems. Connecting one length of pipe to another by flanges is effected by welding. After welding the flanges to the pipe, gaps of about 3.2 to 6.4mm are left between the cement linings of the flanges and adjoining pipes. These gaps have to be filled with a protective coating to prevent seawater attack on the welded carbon steel joints.

One of the local refineries in Kuwait experienced a series of leaks in their cement-lined carbon steel piping seawater-carrying system. These leaks were associated with areas around welded sections near the flanges that were originally sealed with a straight epoxy as specified by the piping contractor. The sealant was applied after mixing 50% epoxy resin with 50% hardener. Inspection of several failed joints revealed various stages of sealant deterioration, including complete removal of the sealant from some welded joints. The majority of these failures occurred on the return seawater line with a temperature of about 60°C.

Because of the design configuration of the piping system, the flow velocity varies from 7fps in some sections of the system to as much as 30fps in others. The reduction of flow velocity in the sections higher than 7fps, cannot be effected without adversely affecting the production process of the plant. The relationship of the rate of erosion damage to fluid velocity is not completely understood, but the damage rate increases to the sixth power of the velocity[1].

Information on the performance of sealants used for the protection of welded joints, particularly in high velocity seawater flow conditions, is rather scanty. Certain plastic coatings had higher erosion resistance and were efficient erosion resistant coatings[2]. The suitability and choice of sealants for shielding the welded joints are dependent on a number of factors. These factors include: adequate surface preparation of the substrate, good adhesive shear strength (bonded characteristics) and erosion resistance of the sealants.

In view of these problems, this investigation was principally directed towards the evaluation of some commercial epoxy-based coating systems used as sealants in seawater. The location and size of the welded gap to be protected made it impractical to use a sand blasting technique for the surface preparation. Therefore, the selected epoxy based coating will be expected to possess excellent adhesion strength under less stringent surface preparation conditions.

The adhesive shear strengths of four different two-component epoxy-based coatings cured at different temperatures were measured according to a standard ASTM method[3]. The erosion resistances of the coatings applied on carbon steel samples were also determined under accelerated test conditions in seawater at 60°C, and at a velocity of 56fps.

Experimental method

Substrate

The specimens used for the adhesive shear strength measurements were hot-rolled mild steel sheets (100mm × 2mm × 24mm). The composition of the mild steel was (in wt %):C-0.25, P-0.04, S-0.25 and Mn-0.3.

The specimens were divided into four batches to be used as: (i) uncleaned (as received); (ii) wire brushed, air-jet, and solvent degreased; (iii) wire-brushed and cloth-wiped; and (iv) chemically cleaned. An inhibited acid de-scaling liquid was used for chemical cleaning.

Sealants

Four commercial two-component epoxy-based products were selected for use as sealants. These sealants were:
(1) A — straight epoxy; Hardner used — bisphenol A.
(2) B — solventless epoxy with dark green pigmented filler; Hardner used — polyamide.
(3) C — solventless epoxy with pastel green pigmented filler; hardner used — polyamide.
(4) D — solventless epoxy with grey pigment; Hardner used — polyamide.

Products B and C contain silica of varying particle sizes as filler material, and with the exception of A, all the products contain different pigments to give varying color shades. The exact constituents of the sealants are not known since they are all commercial patented products.

Effect of curing temperature on adhesion of sealants to steel substrates

Two specimens were selected from each batch of the pretreatment cycle, and the respective sealants were applied over an overlap area of 12.7 ± 0.25mm as recommended by ASTM[3]. The sealant was applied along a sufficient length in an area across the end of both specimens so that a space of approximately 6mm longer than the overlap was covered. The specimens were assembled and held rigidly in a clamping device so that the length of the overlap was controlleld within 0.25mm. The sealant was allowed to cure under controlled temperatures for seven days. The different curing temperatures used in this study were 5, 23, 60 and 80°C, respectively, for each type of sealant. After curing for seven days, the specimens were tested for shear strength of the different sealants by tension-loading according to ASTM method[3], using a tensile testing machine. The rate of top-

loading was maintained at 8-10kg/mm^2/min at a crosshead speed of 1.3mm/min.

Effect of curing at different temperatures and humidities

Batches of specimens were coated with the different sealants and exposed to high and low temperatures, as well as high and low relative humidities for seven days. This method is a slight modification of the ASTM method[4], and the selected conditions were: 23 ± 1°C, 95% RH; 60 ± 3°C, 100% R.H;; 80 ± 3°C, 25% R.H; 23 ± 1°C, 25% R.H.; and 60 ± 3°C, 25% R.H. After the exposure period, the specimens were tested for adhesive shear strength on the tensile testing machine using the conditions recommended by ASTM[3].

Effect of accelerated weathering on the durability of sealants

Hot-rolled mild steel panels of dimensions 150mm × 75mm × 2mm were prepared by wire-brushing and acetone cleaned. Duplicate test panels were coated on one face with the respective sealant material and allowed to cure at room temperature for seven days. The sealants were subjected to accelerated weathering according to ASTM[5], by exposure to UV light (280-315nm) at a rate of 8h/d at 35°C for a period of 27 days in a chamber. Another set of coated test panels was exposed to UV light at 50°C for 60 days.

Accelerated erosion resistance of sealants

The erosion facility used was a rotating disk apparatus[1,2,6] with some modifications made to meet the needs of the specific study. Mild steel samples (70mm × 2mm × 24mm) were used. The samples were cut into two pieces and then joined by electrical arc-welding. Subsequently, the samples were cleaned, coated with the sealants and allowed to cure for seven days under controlled temperatures of 5, 23, 60 and 80°C, respectively. the hardness values for the coated specimens after curing were determined.

Duplicate specimens (eight at one time) were placed diametrically opposite each other on the disk. Filtered seawater, thermostatically controlled at 60°C, was circulated through a test chamber via a pump and a 250gal open fiberglass reservoir.

The disk was rotated in the water-filled chamber at 1440rpm to produce a linear peripheral velocity of 56fps (16.8m/s). The duration of the test period was a maximum of 72h during which specimens were periodically inspected.

Results and discussion

Effect of curing temperature on adhesion of sealants to steel

The average adhesive shear strengths of the sealants under each treatment are shown in Figures 1 and 2. The values represent the average for five samples at the respective curing temperatures. The figures show that as the curing temperature increases, the bonding strength of the sealant to the substrate metals increases, irrespective of the method of surface preparation. In general, there appears to be a gradual increase in the bonding strengths of the sealants with an increase in curing temperature. The effect of curing temperature on the Type C sealant applied to uncleaned substrate (Figure 1) showed a marked increase in bonding strength compared with other sealants. Whereas this level of adhesive shear strength was maintained after the substrate was wire-brushed and cloth-wiped, the adhesive shear

Figure 1

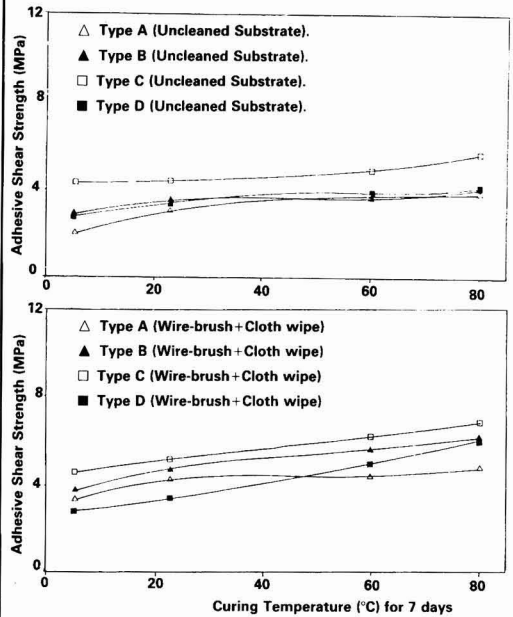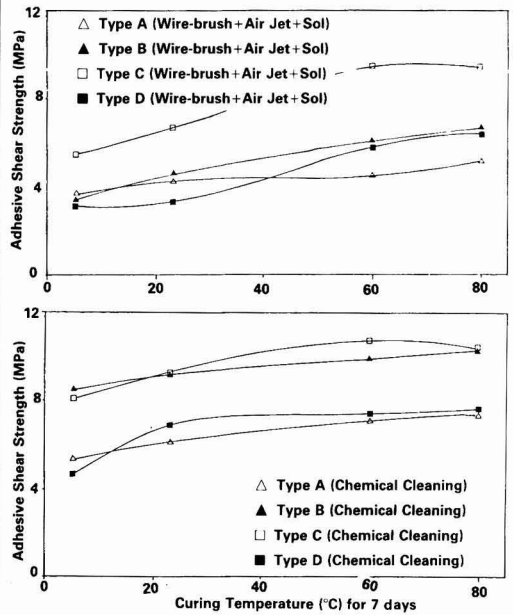Effect of curing temperature on adhesive strength.

Figure 2

Effect of curing temperature on adhesive strength.

strength of sealant type B and D improved to within the same range. Type C sealant showed higher bond strengths at all curing temperatures, except at 5°C after chemical-cleaning (Figure 2), compared with other types of sealants. Sealant
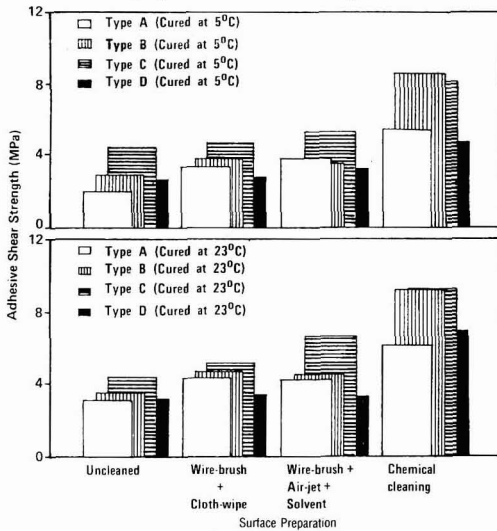
Types B and C showed significantly higher bonding strengths at all curing temperatures when chemically cleaned than those obtained for types A and D sealants. The changes in adhesive shear strengths of the different types of sealants with changes in surface preparation methods are shown in the bar charts (Figures 3 and 4). The bar charts demonstrate the relative sensitivity of the different types of sealants to the steel substrate conditioning and curing temperatures. In general, the sealant types (A, B, C and D) showed a marked

Figure 3

Effect of surface preparation on adhesive strength.

improvement in adhesive bond strength on substrates prepared by wire-brush, air-jet and solvent-clean, and by chemical cleaning. The adhesive shear strength of all the sealants applied after chemical cleaning, however, were significantly higher than those of corresponding samples prepared by any other surface preparation methods. The bonding strength for Type A sealant cured at 23°C was 6.139MPa for the cleaned substrate, whereas for the uncleaned substrate, it was 3.096MPa for Type C sealant cured at 60°C, and the lowest strength was 5,366MPa for Type A sealant cured at 5°C.

Effect of curing at different temperatures and humidities

The test conditions of temperature and humidity, as recommended by ASTM[4], were modified to correspond to local environmental parameters. Table 1 summarizes the effect of curing at different temperatures and humidites on the investigated shear strengths of sealant-bonded mild steel substrates. The results show that curing under low humidity improves the shear strengths of the sealants. At 25%RH, increasing the temperature caused an increase in bond strength, whereas at 95% and 100%RH, a decrease in the bond strength occurred. Table 1 also indicates that the filled epoxy systems of Type B and Type C possess superior bond strength than the unfilled systems (Type A and D) under these conditions.

The addition of filler mateiral to the epoxy system was reported to reduce the susceptibility of the expoxy adhesive to moisture absorption and increase its adhesive strength[7,8]. This may account for the greater bonding strengths obtained for Type B and Type C sealants compared with those observed for Type A sealant under high humidity conditions. The combined effect of temperature and moisture were observed to give rise to residual stresses that are potential sources of dimensional instability of adhesives[8,9].

From the results shown in Table 1, the decrease in bond strength from curing under conditions of high humidity can be attributed to the presence of a weak boundary layer created along the interfaces of the bonded test samples due to diffusion of water through the sealants[10]. Temperature, time of exposure and type of sealant, however, are contributory factors to the magnitude of the decrease in bond strength.

Figure 4

Effect of surface preparation on adhesive strength.
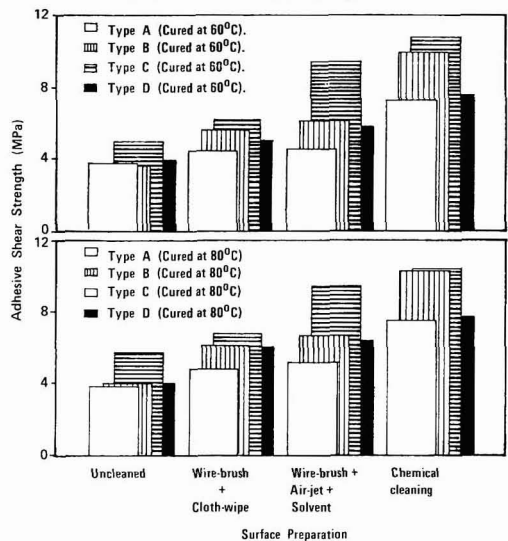
Table 1

Effect of curing at different temperatures and humidities on the adhesive shear strength of sealants.

Surface Preparation	Sealant Type	Coating Thickness (mm)	Adhesive Shear Strength (MPa)				
			23°C 95% RH	23°C 25% RH	60°C 100% RH	60°C 25% RH	80°C 25% RH
Wire brush + Air-jet + Solvent	A	1.8-2.0	3.403	3.810	2.928	4.431	5.877
	B	1.8-2.0	4.575	4.921	3.184	6.182	7.594
	C	1.8-2.0	5.223	5.518	3.801	6.661	7.698
	D	1.8-2.0	3.991	4.151	2.960	5.648	6.571

Effect of accelerated weathering on the durability of sealants

Epoxy coatings are susceptible to hydrothermal degradation and UV degradation. The adsorption of moisture results in a decrease in the glass transition temperature and mechanical properties, which is reversible by drying [11,12], whereas the effects of UV are considered permanent [13].

The effects of exposing the sealants to UV radiation (280-315nm) in an accelerated weathering chamber are summarized in Table 2. Type A sealant was the most affected under exposure to UV irradiation at 30°C. Its colour changed from cream to yellow/orange in the first 24h, became darker after 48h, and remained so until the end of the test period of 27 days. Type B and Type D sealants showed no change in colour, whereas Type C sealant changed colour from pale green to yellowish-green in the first 24h, with no further change up to the end of the test period. Visual examination of the exposed sealant samples after the test period showed no indication of degradation or defect such as cracking or blistering.

As a result of exposure to UV radiation at 50°C, Type A sealant suffered the highest degree of degradation compared with the other sealants (B, C, and D) after 30 days of exposure. Apart from yellowing and chalking, surface crazing of type A sealant was observed. As the exposure time increased, chain scission occurred, and the Type A sealant appeared to degrade more quickly than the other sealants (B, C, and D). At this exposure temperature (50°C), some post-curing with a subsequent increase in crosslink density of the sealant is to be expected when the sample is first exposed [14]. Type C sealant showed a loss in the degree of surface glossiness, change in colour, and some crazing marks, whereas for Types B and D sealants, only a small loss in surface glossiness was observed after the test period.

For practical applications, the surface degradation of epoxy-based systems is important since chalking leads to erosion, and microcracks may lead to crack propagation into the bulk of the sealants when loaded.

Erosion resistance of sealants

The erosion resistance of the different sealants under hydrodynamic conditions are summarized in Table 3. When a sealant is completely removed, as in the case of Type A after 2-4h, it indicates a qualitative condition of gross failure.

It can be seen from Table 3 that Type A sealant showed low erosion resistance compared with all other sealant types tested. This low erosion resistance was reported for epoxy enamel and epoxy paste [2,6]. Unfilled epoxy is not suitable for use under erosion conditions of high intensities, although it can adequately be used as a corrosion resistant coating in areas of no erosion or of low intensity erosion. The high erosion resistance of Type B and Type C sealants can be attributed to the presence of fillers (sillica powder) of varying particle sizes in the polymer matrix. Type C sealant contains much coarser silica particles compared with Type B sealant, and the differences in erosion performance of the two sealants may be due to the differences in particle size and loading of the fillers in the polymer matrix. The erosion resistance of Type D sealant can be classified as moderate in comparison with those observed for Types A, B, and C sealants.

There appears to be some correlation between the adhesive shear strength of the sealants and their erosion resistance. Type B and Type C sealants, which showed high adhesive shear strength (Figures 1 and 2), were more erosion-resistant than Type A. Although no direct relationship between erosion resistance and surface preparation method could be established, the erosion resistance improved when the mild steel substrates were cleaned by wire-brush, air-jet and solvent-clean, as well as when prepared by chemical cleaning (Table 3). In general, chemical cleaning gave the best erosion performance for all sealants tested. This could be due to the improvement in the substrate surface that allowed better wettability of the surface by the sealant [15].

A comparison of the hardness values obtained for the four sealants confirms the effect from the presence of silica in the polymer matrix of both Type B and Type C. Type A sealant is

Table 2

Accelerated weathering of sealants under UV irradiation

Sealant Type	Coating Thickness (mm)	Observations	
		27 days at 30°C	60 days at 50°C
A	4.0-4.25	Colour changed from cream to yellowish/ orange after 48h; no further change till end of experiment.	Change of colour from cream to yellowish/ orange after 24h; deeper yellowish colour after 24h; evidence of crazing marks, chain scission and chalking after 30 days.
B	3.75-4.25	No change in colour.	No definite change in colour throughout. Slight chalking and loss in glossiness after 60 days.
C	3.25-4.25	Slight colour change from pale green to yellow/green after 24h; no further change till end of experiment.	Change in colour from pale green to yellowish-green and crazing marks after 60 days.
D	3.50-4.25	No change in colour	No definite change in colour. Slight loss in glossiness after 60 days.

a softer material (<50R hardness number) than Type B (98R), Type C (160R) and Type D (64R) — Table 3. The marked differences in hardness can also be attributed to the fact that both Type B and Type C contain silica. This difference in mechanical properties is again reflected on the adhesion/erosion performance of Type A under hydrodynamic conditions, which was very poor compared with the other sealants, irrespective of surface preparation method. However, wire-brush, air-jet and solvent-clean are the most practical methods of surface preparation for welded joints inside pipelines.

Conclusions

From the results of this investigation, the following conclusions may be drawn:
1. The presence of moisture during the curing stage of the sealants results in a decrease in shear bond strength.
2. Surface preparation influences the adhesive shear strength and erosion performance of the sealants.
3. Erosion resistance of each sealant is related to its adhesive shear strength.
4. Unfilled epoxy (Type A) has low erosion resistance, and Type D has moderate erosion resistance.
5. Type C and Type B sealants showed higher shear strength and erosion resistance under hydrodynamic conditions than Type A and Type D.
6. Type B and Type C sealants are suitable for protection of welded joints under hydrodynamic conditions (<16 m/s).

Acknowledgements

References

1. Lichtman, J. Z., Kallas, D. H., Chatten C. K. and Cochran E. P. Jr., *Corrosion*, 1961, 497.
2. Kallas, D. H., Lichtman, J. Z. and Chatten, C. K. "Cavitation erosion resistance coatings. Seventh Joint Army-Navy-Air Force Conference on Elastomers Research and Development, Washington D.C. ONR-13, 1962, **2**, 422.
3. ASTM D1002-72. Strength properties of adhesives in shear by tension loading. *ASTM*, Philadelphia, Penn. 1986.
4. ASTM D1183-70. Standard test methods for resistance of adhesives to cyclic laboratory aging conditions. *ASTM*, Philadelphia, Penn. 1986.
5. ASTM D904-57. Exposure of adhesive specimens to artificial natural light. *ASTM*, Philadelphia, Penn. 1986.
6. Lichtman, J. Z., Kallas, D. H. and Rufolo, A. Cavitation erosion facilities and developments at the U.S. Naval Applied Science Laboratory, 1967, **99**(1), 273.
7. Ramaswamy, R. and Achary, P. S., "Effect of a phenol formaldehyde resin on the adhesion of a polysulfide sealant", Adhesive Joints, Formation, Characteristics and Testing. Ed. Mittal, K. L. *Plenum Press*, New York, 1984, 31.
8. Hughes E. J., Boutillier, J. and Rutherford, J. L. "The Effect of Moisture on the Dimensional Stability of Adhesively Bonded Joints", Adhesive Joints, Formation, Characteristics and Testing, Ed. Mittal, K. L. *Plenum Press*, New York, 1984, 137.
9. Chen, W. T. and Nelson, C. W. *IBM Journal of Research and Development*, 1979, **23**(2), 179.
10. Baun, W. L., "The Role of Surface and Bulk Characterization in the Evaluation of Adhesive Joints", Adhesive Joints, formation, characteristics and testing, Ed. Mittal, K. L., *Plenum Press*, New York 1984, 3.
11. Morgan, R. J., O'Neal, J. E. and Fanter, D. C., *Journal Materials Science*, 1980, **15**, 751.
12. Moy, P. and Karasz, F. E., "Polymer Engineering Science", 1980, **20**, 315.

Table 3
Erosion rating of the different sealants at 60°C and 56fps (16.8 m/s) velocity.

Sealant Type	Curing Temp (°C)	Coating Thickness Range (mm)	Hardness Rockwell (R)	Surface Preparation			
				As Received	Wire-brush + Cloth-wipe	Wire-brush + Air-Jet + Solvent	Chemical Cleaning
A	5	1.0-1.5	<50	F-2 h	F-2 h	F-2 h	F-4 h
B		2.0-2.9	98	F-12 h	F-26 h	F-18 h	F-36 h
C		2.0-3.8	160	F-19 h	F-30 h	I-72 h	F-46 h
D		2.0-2.9	64	F-4 h	F-8 h	F-16 h	F-12 h
A	23	1.0-1.5	<50	F-4 h	F-4 h	F-4 h	F-24 h
B		2.0-2.9	98	F-18 h	F-16 h	F-28 h	F-45 h
C		2.0-3.8	160	F-24 h	F-30 h	F-40 h	F-50 h
D		2.0-2.9	64	F-8 h	F-10 h	F-18 h	F-45 h
A	60	1.0-1.5	<50	F-2 h	F-8 h	F-4 h	F-20 h
B		2.0-2.9	98	F-48 h	F-45 h	I-71 h	I-72 h
C		2.0-3.8	160	I-72 h	I-72 h	I-72 h	I-72 h
D		2.0-2.9	64	F-8 h	I-24 h	I-72 h	I-72 h
A	80	1.0-1.5	<50	F-2 h	F-8 h	F-8 h	F-15 h
B		2.0-2.9	98	F-29 h	I-72 h	F-56 h	I-72 h
C		2.0-3.8	160	F-44 h	I-72 h	F-56 h	I-72 h
D		2.0-2.9	64	F-12 h	F-28 h	F-36 h	I-72 h

F = Failed, I = Intact

Corrosion of varnished steel induced by sulphur dioxide and sodium chloride in the atmosphere

by M. Morcillo, L. S. Hernández, E. Otero and S. Feliu, Centro Nacional de Investigaciones Metalúrgicas. Avda. Gregorio del Amo, 8, 28040-Madrid, Spain

Abstract

The paper analyzes the behaviour of a steel/varnish system in atmospheres polluted with SO_2 and/or NaCl, with an emphasis on the quantification of the underfilm corrosion of steel. Concentrations of 0.008% (80ppm) and 0.016% (160ppm) of SO_2 and 0.017% and 5.0% of NaCl were employed in humidity-saturated atmospheres. The tests were run for 500 hours.

The effect of the SO_2 permeated through the varnish film is shown to be decisive for underfilm corrosion of the steel. On the contrary, the NaCl does not interact with the steel due to the low ionic permeabilities of the varnish. In the joint action of both contaminants the underfilm corrosion increases as the SO_2 concentration increases, whereas it decreases as the NaCl concentration in the atmosphere increases.

Introduction

Atmospheric pollution heavily influences the durability of the anticorrosive paint coatings, promoting: (i) the atmospheric corrosion of the metal surface that later receives the organic coating; (ii) the degradation of the film properties during its application and curing; and (iii) the progressive deterioration of the metal/paint system as a consequence of its exposure to atmospheric agents. This paper considers the latter of those effects, i.e. the degradation of the steel/varnish system caused by the contaminants SO_2 and NaCl present in the atmosphere where the system is exposed. It is well-known that the durability of the paint coatings decreases significantly as atmospheric aggressiveness increases. Nevertheless, there are very few studies which quantitatively relate the paint durability with the SO_2 concentration or salinity in real atmospheres[1]. Most of the existing data in the bibliography refer to laboratory studies conducted in accelerated corrosion chambers where the concentration of pollutants is excessively high. For example, in the Kesternich test (DIN 50018) SO_2 concentrations of up to 7,000ppm are used, whereas in industrial atmospheres highly contaminated with SO_2 the concentration of this gas rarely exceeds 1ppm[2]. Fewer still are the studies considering the joint action of the pollutants SO_2 and NaCl ever though this is a frequent situation in practice (industrial zones near the coast).

The present research studies the effect of continuous exposures to atmospheres contaminated with SO_2 or NaCl, and to both atmospheres (in alternate exposures), in the decay of a steel/varnish system. The underfilm corrosion of the steel base is mainly considered from a fundamental point of view, in order to arrive at a better understanding of the corrosion process, as well as the mechanistic aspects involved. In this way a model coating of a very low thickness (3μm) was applied over flat steel plates. The painted specimens were then exposed to controlled atmospheres polluted with SO_2 and NaCl.

The concentrations of SO_2 in the atmosphere, 80 and 160ppm, are, with relation to Kesternich test, an attempt of approximation to real conditions, although they remain distant enough to be not directly applicable to practical situations.

Experimental

From a flat cold rolled mild steel plate 0.5mm thick, 5×5cm specimens were prepared. After degreasing with trichlorethylene they were weighed on an analytical balance with a precision of 0.1mg. Then a vinyl "strippable" varnish film, 3μm dry thickness, was applied by means of a wire-wound rod. After a week of curing at room temperature, the edges of the specimens were protected by dipping in a melt mixture of wax and paraffin.

For the exposure to SO_2 polluted atmospheres a GK 500 chamber (Teletric Corporation) which employs mixtures of humid air and SO_2 was used. The temperature inside the chamber was maintained close to 25°C, with the relative humidity being between 95 and 98%. The SO_2 was of 99.9% purity and the air flow 500l/hr. Two atmospheres were considered: one with a SO_2 concentration of 0.008% (80ppm), and the other with 0.016% (160ppm).

A salt fog chamber (Erichsen, model 351) was employed for the exposure to NaCl polluted atmospheres. The temperature inside the chamber was kept between 20 and 25°C and the condensation level was maintained to 1-2 ml/hr, as according to ASTM B-117. The concentrations of sodium chloride in the saline solution were 0.017% and 5.0%. Within this paper the resulting atmospheres will be designated by the corresponding concentration of the saline solution used.

Two types of running tests were carried out: "continuous exposure" up to a total of 500 hours in atmospheres with either SO_2 or NaCl, and "alternate exposure" to both types of atmospheres for 10 cycles. Each test cycle consisted of a 24 hour exposure in the SO_2 contaminated atmosphere followed by another 24 hour exposure in the NaCl contaminated atmosphere.

Various series of specimens were prepared and removed from the test chambers at different times of exposure. Unpainted steel specimens were simultaneously exposed as controls. One series of specimens was prepared for the determination of the underfilm corrision of steel. Once the specimens were withdrawn from the test chambers, the varnish film was peeled off and the steel support placed in an inhibited hydrochloric acid bath to remove the corrosion products. Then, the steel plate was weighed in order to check for weight loss (corrosion).

The other series of specimens were employed for the analysis of corrosion products and electrochemical measurements. The former was done by X-ray diffraction. The technique and the equipment employed for the electrochemical measurements have been described in a previous paper[3].

Permeability measurements

For the determination of the permeation rates of water vapour and oxygen through the varnish coating, free films of the coating material to a dry film thickness of 3μm were prepared.

The permeability of the water vapour was carried out by means of permeability cups, using a gradient 100/0 of relative humidity. The temperature was kept constant at

Table 1

Water vapour permeability of varnish films, 100 μm thickness. Data compiled from references 6 and 7.

Varnish	Water vapour permeability ($gH_2O.cm^{-2}.d^{-1}$)	Ref.
Melamine resin (water soluble)	4.8×10^{-3}	6
Polyurethane	1.4×10^{-3}	6
Alkyd melamine	1.2×10^{-3}	7
Phenolic resin	1.1×10^{-3}	6
Chlorinated rubber	1.0×10^{-3}	6
Epoxy polyamide	1.0×10^{-3}	7

Table 2

Permeability to oxygen of varnish films[8], 100 μm thickness. Temperature: 20°C.

Varnish	Oxygen permeability ($g\ O_2.cm^{-2}.d^{-1}$)
Cellulose nitrate	1.06×10^{-4}
Alkyd melamine resin	1.03×10^{-5}
Epoxy resin	0.73×10^{-5}
Vinylchloride/vinylacetate 87/13 copolymer, air dried	0.75×10^{-5}
Chlorinated rubber	0.22×10^{-5}

20°C. The average value of six measurements was $11.86 \times 10^{-3}g.cm^{-2}d^{-1}$.

For the oxygen permeability measurements the electrochemical technique was followed, employing a selective oxygen electrode[4,5]. The free film was located in a permeation cell between two compartments, one with distilled water kept constantly saturated with oxygen, and the other with de-aerated distilled water in which an Orion selective oxygen electrode (model 97-08) was placed. The water in both compartments was maintained at $20 \pm 1°C$. The readings of the oxygen transferred through the varnish film were taken with an Orion Analyzer-Processor, model 901. The average value of six measurements was $1.239 \times 10^{-3}g.cm^{-2}d^{-1}$.

In Tables 1 and 2 water vapour and oxygen permeabilities obtained by other researchers with different varnish films, 100μm thickness, are compiled. They show permeation rates much lower than ours. The lower thickness of our films and possibly the presence of film defects at such a low thickness might explain the relatively high water vapour and oxygen permeation rates found.

Results

Corrosion of steel beneath the varnish film

Tables 3 and 4 illustrate the results of the weight loss (corrosion) of the steel, both unpainted and painted, at different times of exposure in diverse atmospheres. The

Table 3

Corrosion of steel, in mg/cm², uncoated and coated with a varnish coating (3μm thickness) in continuous exposure to different atmospheres.

Atmosphere	Steel Condition	Time of exposure, days					
		1	2	6	10	15	21
SO₂, 0.008%	Uncoated	—	2.11	2.75	3.23	4.16	5.20
	Coated	—	0.40	0.94	1.37	1.42	1.70
SO₂, 0.016%	Uncoated	1.23	2.36	6.00	10.68	20.20	28.00
	Coated	0.38	1.03	1.26	2.76	3.36	4.14
NaCl, 0.0017%	Uncoated	—	6.77	14.70	18.06	20.00	21.46
	Coated	*	*	*	*	*	*
NaCl, 5%	Uncoated	—	5.86	14.20	21.60	30.05	38.52
	Coated	*	*	*	*	*	*

* Corrosion products on the steel surface are not visually observed and gravimetric measurements do not show any significant weight loss of steel.

Table 4

Corrosion of steel, in mg/cm², uncoated and coated with a varnish coating (3μm thickness) in alternating exposure to different atmospheres.

Atmosphere	Steel Condition	Number of cycles*					
		1	2	3	5	8	10
SO₂, 0.008%/NaCl, 0.017%	Uncoated	3.49	5.19	5.42	5.91	7.77	16.03
	Coated	1.14	1.40	—	—	—	—
SO₂, 0.008%/NaCl, 5.0%	Uncoated	4.29	5.85	6.90	8.76	16.03	18.32
	Coated	0.23	0.48	0.61	1.19	1.76	4.35
SO₂, 0.016%/NaCl, 0.017%	Uncoated	3.23	7.46	19.82	32.66	51.00	79.10
	Coated	1.80	3.53	8.12	14.00	17.52	23.52
SO₂, 0.016%/NaCl, 5.0%	Uncoated	4.23	7.00	7.90	12.07	16.27	19.57
	Coated	1.05	2.79	4.12	5.48	7.20	8.05

* 1 cycle = 24 hours of exposure to the atmosphere with SO₂ + 24 hours of exposure to the atmosphere with NaCl.

presence of the varnish coating obviously reduces the corrosion of the underlying steel. However, in certain situations (the most unfavourable ones), this reduction does not represent more than 20-30%.

It must be pointed out that there is an absence of underfilm corrosion in the NaCl polluted atmospheres. On the contrary, in the SO$_2$ polluted atmospheres underfilm corrosion increases as the concentration of SO$_2$ in the atmosphere increases too; a direct relationship between underfilm corrosion and SO$_2$ content in the atmosphere has been found.

Film deterioration and nature of the corrosion products

In the exposure to SO$_2$ polluted atmospheres the films rapidly develop small blisters that are uniformly spread over the entire surface of the specimen. The blister size increases slightly as the SO$_2$ content in the atmosphere increases. The blister size also increases with the exposure time.

A simple visual inspection, however, cannot detect breakage of the blisters over the 500 hours of exposure. The corrosion products formed under the varnish film had a brown colour and were constituted exclusively of α-FeOOH (goethite).

In the NaCl polluted atmospheres the varnish film remains intact after 500 hours of exposure. No rust formation on the steel was detected.

In the alternate exposure to both atmospheres the deterioration of the varnish film in the first cycles of exposure is similar to that of the continuous exposure to SO$_2$ polluted atmospheres, however, as the exposure time increases the blisters burst, permitting the outset of corrosion products. These products, that had a brown colour when they were beneath the film, change to a reddish colour when they leave the blister. Even when the corrosion products are mostly constituted by α-FeOOH, a certain amount of Fe$_3$O$_4$

(magnetite) was detected along with traces of γ-FeOOH (lepidocrocite) in the most corroded samples.

Impedance measurements

Figure 1 illustrates the Nyquist diagrams for the steel/varnish system once weathered in the different atmospheres. The graphs also indicate the ionic resistance and the capacitance of the varnish film calculated from the high frequency zone of the diagram[9].

From the aforementioned values it may be inferred that the exposure to the NaCl polluted atmospheres hardly alters the varnish coating. The film ionic resistance and the film capacitance maintain their initial values; the Nyquist diagrams show a practically capacitive behaviour.

In the remaining atmospheres the ionic resistance of the varnish film decreases notably in the first days of exposure, the greatest decrease being in the atmospheres with a higher SO$_2$ content. The capacitance of the film, however, do not undergo great changes.

Discussion

The corrosion of painted metals, as with bare metals, follows a mechanism of electrochemical nature. There are, however, two main differences: the reactants must go through the paint film to enter into contact with the metal, and the corrosion process is restricted to the narrow interfacial region[10].

In neutral media, oxygen and water must pass through the paint film for sustaining the cathodic reaction of oxygen reduction. Besides, for significant corrosion to take place, a conductive ionic phase must be constituted at the interphase metal/paint. This phase will facilitate the ionic transport between the anodic and cathodic zones on the metallic surface[3].

Figure 1

Nyquist diagrams for the steel/varnish system once weathered in the different atmospheres.
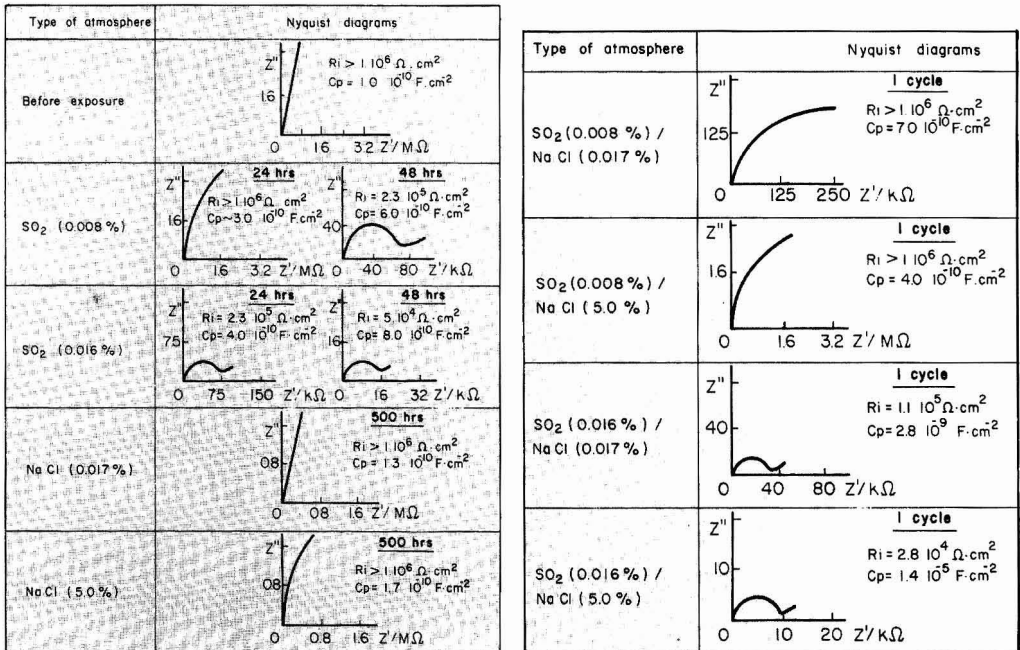
The ionic component of this conductive phase can come either from existing hydrosoluble residues on the metallic surface (before painting), as was shown in an earlier study[3], or from hydrophilic compounds of the paint formula, which are lixiviated and dragged towards the interphase as water ingress through the coating thickness. When the metal/paint system is exposed to polluted atmospheres, the constitution of such an ionic phase will depend upon the possibilities to which the aggressive agents of the atmosphere can enter into contact with the metallic surface.

The kinetic of the corrosion process under the paint film also will depend on the possibilities of the corrosion products to diffuse outside the interphase. In this sense the adhesion of the paint film to the metallic support should play an important role, which still has not been clarified[11].

The corrosion of the base metal will induce blisters, delaminations or loss of adhesion of the paint film with relation to the metal surface. Once the coating has been perforated by the corrosion products accumulated in the metal/paint interphase, the aggressive chemicals of the atmosphere can directly interact with the metallic surface without having to permeate through the paint film.

To study the mechanisms of corrosion of painted steel exposed to contaminated atmospheres[12], it was considered interesting to use a paint coating with the following characteristics: (i) very low thickness, which would facilitate a faster penetration of the aggressive agents of the atmosphere, enabling a significant corrosion of the base metal in a test time of reasonable length, and (ii) not pigmented, nor containing hydrophilic components that could interfere with the corrosion process under study. To comply with these characteristics a vinyl "strippable" varnish coating was formulated. Its transparence also permitted the visual observation of the corrosion process in the interphase from outside, and its low adherence facilitated the collection of the corrosion products for their posterior identification.

Permeation of SO_2 through the varnish film

From the observation of Table 3 it can be inferred that significant corrosion of the underlying steel takes place when the system is exposed to atmospheres containing SO_2. To what can this attack be attributed to?. The following three possibilities can be considered:

(a) Severe deterioration of the coating by the SO_2, which enables the posterior direct attack of the steel by the aggressive agent. The heavy absorption of the SO_2 in many polymeric materials that constitute the vehicle in anticorrosive paints is well-known (e.g., in epoxy paints the solubility of SO_2 can reach up to 20-30% in weight[13]. The absorbed SO_2 can react with the hydrocarbon groups (RH) of the polymer, giving rise to sulfinic acids ($RHSO_2$) and sulfonic acids ($RHSO_3$)[14].

This severe deterioration of the varnish films, at least during the first days of exposure, is not inferred from the visual observation of the coating exposed to the SO_2 atmospheres, as well as from impedance measurements (Figure 1). The moderate decrease of the ionic resistance values of the varnish film as the SO_2 content in the atmosphere increases seems to suggest a certain deterioration of the film at microscopic scale. The higher oxygen permeation rates found in weathered free films seems to corroborate such a deterioration.

(b) The stimulation of the corrosion process under the coating by the permeation of SO_4^{2-} ions towards the steel/varnish interphase. To corroborate this point free films of the varnish were exposed between two compartments of a permeability cell. One compartment contained a concentrated solution of H_2SO_4 and the other had distilled water. The permeation of SO_4^{2-} ions and, therefore, of H^+

through the film, would result in a decrease of pH in the compartment of distilled water. No change of pH was observed after 8 hours of contact with the solution, even at 5N concentration of sulphuric acid, which indicates the low permeability of the paint films to SO_4^{2-} ions, as has been reported by other researches[13,15].

(c) SO_2 permeation through the coating in a gaseous state and/or dissolved in water. The chemical nature of the sulphur that permeates through the paint film is open to question: SO_2 in gaseous form, SO_2 dissolved in water, the not dissociated fraction from the H_2SO_3, etc. Because of the above-mentioned reason, an ionic penetration of dissociated fractions from H_2SO_3 or H_2SO_4 must be discarded. According to Svoboda[16], the SO_2 dissolved in water can exist in molecular form over a long period of time, while coexisting with a small fraction of H_2SO_3, very weakly dissociated. Therefore, SO_2 penetration as a gas and/or dissolved in water is feasible. The few available data in the bibliography about

Table 5

SO_2 permeation rate through paint films. Data compiled from references 13 and 17.
Temperature: 23°C.

Paint	Dry film thickness (μm)	Permeation rate ($gSO_2.cm^{-2}.d^{-1}$)	Ref.
Cellulose nitrate	100	4.05×10^{-2}	17
Alkyd resin	88	2.0×10^{-2}	17
Vinylchloride/Vinylacetate copolymer	77	1.1×10^{-3}	17
Butyl methacrylate	40	15.1×10^{-2}	13
Alkyd melamine	50	2.7×10^{-2}	13
Acrylic/polyurethane	70	3.2×10^{-2}	13
Alkyd, medium oil	75	1.8×10^{-2}	13

Table 6

Permeation of chloride ion through varnish films. Data compiled from references 15, 18 and 19.

Varnish	Dry film thickness (μm)	Permeation ($gCl^-.cm^{-2}.d^{-1}$)	Ref.
Cellulose nitrate/ alkyd resin	50	0.35×10^{-6}	18
Neoprene	50	0.85×10^{-6}	18
Epoxy resin	50	0.71×10^{-6}	18
Cellulose acetate	50	22.0×10^{-6}	18
Pentaerythritol alkyd resin modified with linseed oil	75	0.13×10^{-6}	15
Epoxy polyamide	100	0.17×10^{-6}	19
Alkyd	100	0.62×10^{-7}	19
Phenolic	100	1.70×10^{-8}	19

Table 7

Permeation rates of SO_2, O_2 and H_2O through the varnish film (3μm thickness). Estimated consumptions from corrosion rates and obtained by permeability measurements.

	Estimated conumption from corrosion data ($g.cm^{-2}.d^{-1}$)	Permeation rate through free varnish films, 3μm thickness ($g.cm^{-2}.d^{-1}$)
SO_2	4.4×10^{-4}	About 10^{-2} (estimated from data of Table 5)
O_2	0.27×10^{-3}	1.2×10^{-3}
H_2O	1.8×10^{-4}	1.2×10^{-2}

the permeability of SO_2 through paint films (Table 5) suggest high permeation rates of this gas, in the order of 10^{-2}-10^{-3} g.cm^{-2}.d^{-1}.

Permeation of NaCl through the varnish film

In contrast to what accounted for the SO_2 polluted atmospheres, the exposure to NaCl contaminated atmospheres, even at as high NaCl concentration as 5%, did not show any appreciable attack on the underlying steel after 500 hours of testing (Table 3).
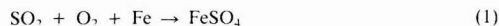
An earlier study[3] demonstrated that for an active corrosion process under the paint film two conditions were needed: (i) the presence of oxygen and water at the metal/paint interface; and (ii) the existance of a conductive phase that provides the ionic conduction between the anodic and cathodic zones of the metal surface. In the case of exposures to atmospheres containing NaCl, it would be the entrance of the Cl^- and/or Na^+ ions through the varnish film that would cause an increase in the ionic conduction at the interface. However, this is not feasible due to the low ionic permeabilities, and in particular to the chloride ion (Table 6), that the paint films present.

So, it is therefore possible to understand the inappreciable underfilm corrosion of steel exposed to atmospheres containing NaCl.

Corrosion of the steel beneath the varnish film

The rusting under the varnish film must occur by a similar mechanism to that which takes place on the unpainted steel exposed to atmospheres contaminated by SO_2[1].

After an initial formation of ferrous sulphate by the reaction of sulphur dioxide with the steel

$$SO_2 + O_2 + Fe \rightarrow FeSO_4 \qquad (1)$$

Figure 2

Evolution of steel corrosion under the varnish film during the first cycle of alternating exposure to different atmospheres.

the hydrolysis of $FeSO_4$ leads to the formation of rust and to the regeneration of the SO_2 as sulphuric acid. Corrosion progresses in the steel/varnish interfacial region even without new SO_2 coming in from outside, due to the well-known cyclic process of rusting.

$$2\,FeSO_4 + O_2 + 2\,H_2O \rightarrow 2\,FeOOH + 2\,H_2SO_4 \qquad (2)$$
$$2\,FeSO_4 + 2\,H_2O \leftarrow 2\,Fe + O_2 + 2\,H_2SO_4 \qquad (3)$$
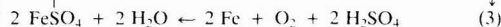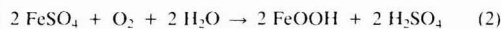
In accordance with Eqs. [1]-[3], the formation of rust will depend on the arrival of SO_2, O_2 and H_2O to the steel/varnish interface. Table 7 may help to know which of these three chemicals species control the corrosion process. The table shows the theoretical consumptions of these species as calculated from the experimental weight loss data (Table 3) of the steel under the coating after the first day of exposure to SO_2 atmospheres. It shows also the permeation rates through free varnish films.

With relation to the water and sulphur dioxide, the permeation rates are far superior to the estimated values (approx. by two orders of magnitude). However, the data for the oxygen fits quite well, which seems to indicate that the arrival of oxygen to the steel/varnish interphase, permeating through the varnish film, is the controlling factor of underfilm corrosion.

Effect of alternate exposures to atmospheres containing SO_2 and NaCl respectively

In alternate exposures of the system to atmospheres containing SO_2 and NaCl respectively (Table 4), the corrosion of steel increases as the SO_2 concentration increases, whereas it decreases as the NaCl content in the atmosphere increases. This fact is graphically shown in Figure 2 where the corrosion due to the first 24 hours exposure to the SO_2 contaminated atmosphere and the total corrosion obtained after the first test cycle (which includes also a second exposure of 24 hours to the NaCl polluted atmosphere) are shown.

Corrosion of steel increases as the SO_2 content of the atmosphere increases, analogously to how it occurred in continuous exposure to SO_2 polluted atmospheres. But corrosion of steel also increases during the subsequent period of exposure to the atmospheres containing NaCl, something that did not occur in continuous exposure to NaCl contaminated atmospheres, where corrosion was inappreciable. How to justify this peculiar behaviour? The first exposure to the SO_2 polluted atmosphere promotes the formation of ferrous sulphate on the steel surface (Equation [1]). The hydrosoluble nature of this compound, already pointed out in an earlier study[3] induces the entrance of water, by osmosis, through the varnish film, even during exposure to the NaCl polluted atmosphere. The repeated formation of rust caused by the above mentioned cyclical process (Equations [2] and [3]) would explain the high corrosion rates found in such situations.

Figure 2 also shows that corrosion of steel is higher at the lowest NaCl content in the atmosphere. It seems probably that the water penetration towards the interfacial region is favored in the atmospheres with a lesser NaCl content, where the water activity on the varnish film is higher. It seems paradoxical that there is inhibition of the underfilm corrosion process as the saline content of the atmosphere is increased, which is just the opposite to what occurs to bare steel exposed to marine atmospheres[20]. If these results could be extrapolated to practical situations, the industrial marine atmospheres would promote more underfilm corrosion as they got further away from the coast.
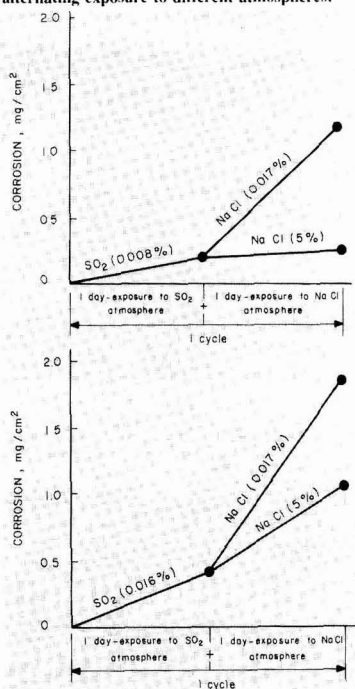
The resistance of paint and varnish films as measured by D.C. and A.C. techniques

by G. T. Burstein, G. Gao and J. E. O. Mayne, Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

Abstract

The resistances of a number of paints and varnishes, both in the form of free films, and as coatings on mild steel, have been measured using a.c. and d.c. techniques. The resistances as measured by both techniques were the same for protective high impedance coatings. A.C. measurements made on painted steel on which corrosion was observed beneath blisters, were resolvable into two components.

In the absence of corrosion either a.c. or d.c. methods may be used to measure the resistance of paint coatings.

Introduction

In 1948 Bacon, Smith and Rugg[1], using a d.c. technique, measured the resistance of over 300 paint coatings immersed in sea-water, and concluded that for good performance, a coating should have a resistance of more than $10^8 \Omega cm^2$. Coatings having reisistances in the range 10^6-$10^8 \Omega cm^2$ were unreliable and those whose resistances were less than $10^6 \Omega cm^2$ behaved poorly.

A comparison of d.c. and a.c. methods of measuring resistance was made by Buller et al[2] and it was reported that at a fixed frequency of 1592 Hz the resistances of detached films were always lower when measured using a.c. Further measurements covering the frequency range 200Hz to 20kHz with free films and films supported on mild steel and platinum showed a steady fall in resistance with increase in frequency. However, analysis of the data of Buller[3] shows that in this frequency range the impedance is dominated by the capacitive component. Extraction of the resistive component from this frequency range is extremely difficult and unlikely to be achieved with a sufficient degree of accuracy; the reported resistances must be regarded as containing a significantly large residual capacitive component.

Callow and Scantlebury[4-8] published a series of papers dealing with a.c. measurements of paint coatings in neutral and acidic solutions. Their most resistive films gave resistances of the order of $10^6 \Omega cm^2$ and consequently suffered rapid breakdown which they were able to follow as it progressed.

The object of the work reported here was to compare the use of d.c. and a.c. techniques for the measurement of the resistance of polymer films.

Experimental

Preparation of free films

An investigation into the cross-linking of epoxy resins by polyamines was in progress; consequently cast films were available with resistances varying from 10^6-$10^{12} \Omega cm^2$. The films were prepared by casting the paint or varnish onto the adhesive side of a gummed paper label, 14 × 9 cm which was resting on a glass plate, 23 × 10 cm, by means of a spreader bar with a gap of 0.006 inch (150μm). The coatings were stored under a filter paper screen for at least two weeks. The paper was then soaked in water, the film removed, dried and mounted in cells, as shown in Figure 1, by means of Dow Corning Silastic 738. This was allowed to cure for two days, after which the cells were filled with 0.1M KCl.

Figure 1

Cell used for measurement of electrical properties of free paint films sandwiched between two half-cells, each containing Ag/AgCl/0.1M KCl.
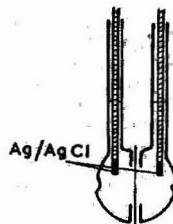

Preparation of supported films

Mild steel specimens, 10cm × 10cm × 0.2cm, were lightly abraded with emery paper (Oakley Grade 3), cleaned by swabbing with xylene, dried and coated with a paint by means of a 0.006inch (150μm) spreader bar and then stored under a filter paper screen for at least two weeks. Three half-cells were then attached to the painted surface, as shown in Figure 2, by means of Dow Corning Silastic 738, which was allowed to cure for two days. The cells were then filled with 0.1M KCl. the specimen area over which measurements were made was ~1 cm².

Figure 2

Cells used for measurement of electrical properties of supported paint films. The half-cells each contain Ag/AgCl/0.1M KCl.
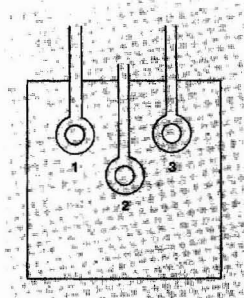
Measurement of D.C. resistance

In the case of the free films two Ag/AgCl electrodes were inserted into the arms of the cell and the resistance of the film measured by means of a Keithley electrometer, Model 610C. The leads to the cell were reversed and a further reading taken and the average of the two readings was recorded as the resistance of the film.

The resistances of the attached films were first measured across the cell/metal interface and then from half-cell to half-cell; this gave rise to six measurements, i.e. 1 : 2, 2 : 1, 1 : 3, 3 :1, 2 : 3, 3 : 2, where the numbers refer to the half-cell numbers given in Figure 2. The measured value for each pair of half-cells was taken to be the sum of the resistances of the two coatings.

In order to determine the limit of measurement by the electrometer the leads were removed and a measurement made; a resistance of $3 \times 10^{13}\Omega$ was recorded and this was taken to be the highest resistance measurable by the instrument.

Measurement of the A.C. impedance

The a.c. impedance of the detached epoxy coatings was measured as a function of frequency using a Solartron 1250 frequency response analyser connected to the two Ag/AgCl/0.1M KCl electrodes via a potentiostat (Solartron 1286). One electrode functioned as working electrode and the other functioned as both counter and reference electrode. With the potentiostat set to 0V, no d.c. current flows through this cell and the Ag/AgCl electrodes are unpolarised. Under application of the a.c. perturbing voltage, only at very high frequencies was the measured value of the modulus of the impedance sufficient to cause polarisation of the Ag/AgCl electrodes. Even in this region however, which is of little interest in the present studies, no effect of the Ag/AgCl electrodes on the measured frequency response could be observed. This feature was examined further by measuring the frequency response of the impedance using several different amplitudes of the a.c. perturbing voltage.

The a.c. impedance of the painted steel specimens described above (Figure 2) was also measured via the three half cells, again using one Ag/AgCl/0.1M KCl electrode as both counter and reference electrode. The working electrode terminal was then connected either to the metal giving a cell-to-metal measurement, or to another Ag/AgCl half-cell giving a cell-to-cell measurement. In the former case the open circuit potential of the metal was -10 to -20mV relative to Ag/AgCl/0.1M KCl; thus application of 0V from the potentiostat gave negligible polarisation.

The frequency response for each specimen was measured over the range 65kHz to $\sim$ 1mHz in 5, 7 or 10 steps per decade of frequency using 3 or 5 cycles per measurement; the lowest frequency limit of measurement was set by the frequency response itself. The amplitude used was determined by the resistance of the paint and the lower current limit of the potentiostat (0.1 to 1nA). For resistances $\sim 10^6\Omega$ an amplitude of 5mV rms (7mV peak) gives a maximum current variation of $\pm$ 7nA at low frequency. For the highest measured resistances of $\sim 10^{11}\Omega$ (see below) amplitudes of up to 6.5V rms (9.2V peak) were used producing maximum current variation at low frequency of $\sim$ 0.1nA. Whilst application of high a.c. perturbing voltages is not common within the context of corrosion, in the present systems it is most appropriate, providing the perturbing voltage does not itself affect the impedance. This feature was checked by variation of the applied a.c. voltage, and re-checked by comparison of the resistance as measured by a.c. response at low frequency with the d.c. resistance. Impedances greater than $\sim 10^{11}\Omega$ could not be measured accurately with the present system since this approaches too closely the input impedance of the potentiostat. It is a viable technique provided it is demonstrated that the perturbing voltage does not itself alter the nature of the interface and the steady state nature of its reactions. These properties are in fact determined by the current flowing, rather than by the magnitude of the voltage used to generate the current. The effects can be checked as follows.

(i) Since corrosion of painted steels is an irreversible phenomenon, and necessarily leads to reduction of the interfacial resistance, measurement of the impedance spectrum more than once at the same amplitude should provide irreproducible data, with a progressive change in the magnitude of the resistive components if the steady state nature of the interfacial reactions is affected by the applied voltage.

(ii) If the applied voltage affects the reactions, the frequency response spectrum is expected to be a function of that voltage. Otherwise, only the scatter observed at low frequencies is affected.

(iii) The frequency response spectrum can be measured with the specimen polarised by application of a superimposed polarising potential. This spectrum should show resistive components different from those measured in the absence of polarisation if the nature of the interface is affected by the polarising potential.

All these methods were tested for the present data.

Results

An impedance spectrum of a typical detached epoxy resin is presented in Figure 3 in terms of log $|Z|$ vs log ω (Figure 3a) and φ vs log ω (Figure 3b) where ω, φ and Z are the frequency, phase angle and impedance respectively. This diagram (the Bode plot) demonstrates that the detached film can be described electrically as a simple parallel network of a capacitance (at high ω) and a resistance (at low ω). The gradient of the capacitive region, $\partial \log |Z|/\partial \log \omega = -0.90$, a little less negative than the value of -1 anticipated for a pure capacitor; this leads to a value of φ of a little less than $90°$ in the capacitive region of Figure 3b. There is no evidence of any second component of the simple network. The same data are presented in Figure 4 as Z'' (the imaginary component of the impedance) as a function of Z' (the real

Figure 3

Bode plots of the impedance of paint C. 0V d.c., 0.1V(rms) a.c. (a) log $|Z|$ vs. log ω, (b) φ vs. long ω.
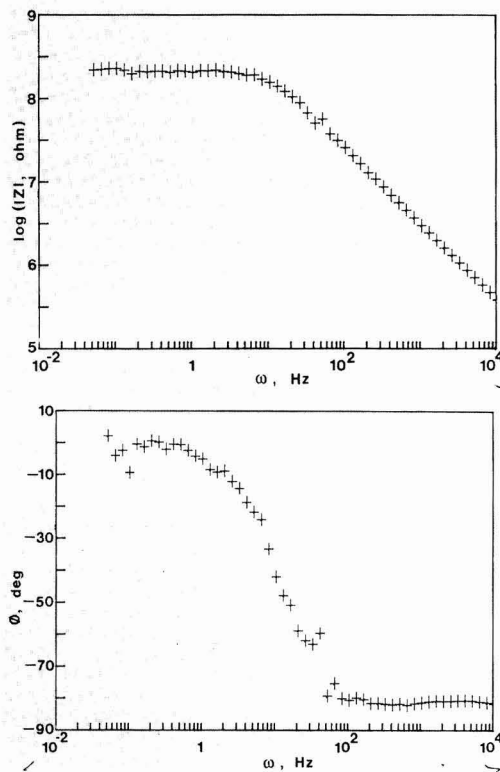
component of the impedance), representing the Nyquist plot. A single semicircle is seen, representative of the simple equivalent circuit described above. Both Figures 3a and 4 give the resistance, R of the epoxy resin film as being 2.2×10^8 Ω, and the capacitance, $C = 63$ pf (measured at 1000Hz). The value is 100 pf measured at 1Hz. Because the gradient of Figure 3a at high ω deviates slightly from -1, all capacitances quoted are those measured at $\omega = 1$kHz, using $C = 1/2\pi$ $\omega |Z|$. However, the error introduced by calculating C at a specific frequency is small; over the frequency range 10mHz to 65kHz (the maximum frequency applied) the variation in C is a factor of 2.4.

Figure 4

Nyquist plot of the impedance of the paint shown in Figure 3.
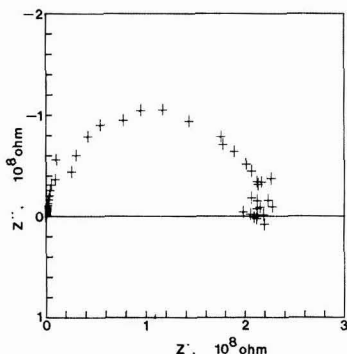
To demonstrate the effects of the applied a.c. voltage Figure 5 shows the Bode plot of one epoxy resin measured at 0.2V(rms), and at 0.8V(rms). The ordinate has been shifted by an order of magnitude for the two plots to allow distinction of the data. It is seen that the magnitude of the impedance is independent of the applied amplitude. Only the scatter observed at low frequency is significantly reduced by increasing the amplitude.

Figure 6 shows the effects of applying a d.c. bias across a detached epoxy resin film. There is a small reduction in resistance as the d.c. bias is increased, but no change in

Figure 5

Bode plots of the impedance of paint D measured at different applied a.c. voltage. 0V d.c. (a) log |Z|, 0.2V(rms) a.c., (b) long 10|Z|, 0.8V(rms) a.c.
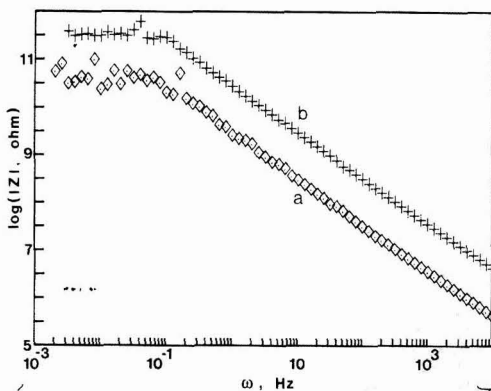
capacitance. The observed reduction in resistance is completely reversible, however, in that removal of the d.c. bias returns the resin to its original resistance. An expanded discussion of the effects of an applied d.c. bias will be given in a subsequent communication.

The resistances and capacitances of the series of detached epoxy films, as measured by frequency response analysis, are listed in Table 1, together with the conditions under which they were measured. Also listed in Table 1 are the resistances of the same detached films as measured by d.c. using the electrometer, and they are in excellent agreement with the a.c. values. Table 1 also shows that the effect of the a.c. amplitude and the d.c. bias are negligible. No a.c. measurements are presented for film F (see Table 1) since this exceeds the maximum resistance measureable by the FRA using an amplitude of 6.5V rms; it was found that the frequency response spectrum for this film was identical to that achieved with the potentiostat leads (with the reference and counter electrode leads short-circuited) in open circuit in air. Using the maximum amplitude available via the potentiostat, it appears that the maximum resistance measurable by the FRA is $\sim 3 \times 10^{11}$ Ω in this configuration.

Figure 6

Bode plots of the impedance of paint c measured at different applied d.c. voltage. 0.1V(rms) a.c. (a) log |Z|, 0V d.c., (b) log 10|Z|, 1.0V
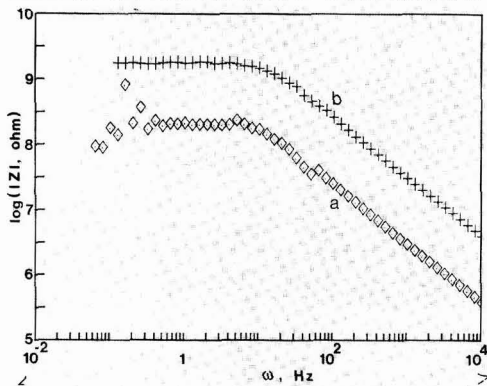
Measurements of the impedance of supported paint coatings were similar in form to those given in Figures 3-6. They were made separately from cell to metal (using the metal substrate as the working electrode), and from cell to cell, as described above. For cell-to-metal measurements, data achieved potentiostatically are equivalent to open circuit data if and only if it can be demonstrated that the applied d.c. potential causes negligible applied polarisation. Thus for each of these systems, the open circuit potential was measured prior to frequency response analysis. It varied between -30 and -10mV (relative to Ag/AgCl/0.1MCl⁻), and application of 0V (Ag/AgCl/0.1MCl⁻) provided no observable current flow. For cell-to-cell measurements, no polarisation can occur. Typical results of both types of measurement are presented in Figures 7 and 8. Again, each system can be described as a single parallel network of a resistance and capacitance. The technique is unable to resolve the metal/paint interface as a distinct component of the equivalent circuit. It is also unable to resolve the separate components of the two-coat system (zinc chromate primer plus finishing coat), as shown in Figure 8.
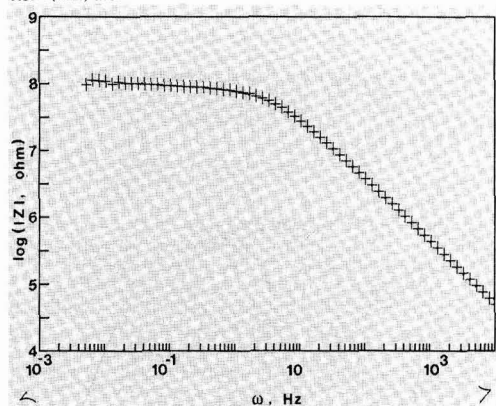
The numerical values of the components for the supported films are listed in Table 2, together with the measured d.c.

resistances. Again, the resistances measured by the a.c. and d.c. techniques are in excellent agreement. Moreover, the table demonstrates, as expected, that the impedance determined by the cell-to-cell measurement is approximately equal to the sum of the impedances of the appropriate cell-to-metal measurement: i.e. $R_{ab} = R_a + R_b$ and $1/C_{ab} = 1/C_a + 1/C_b$ where a and b are the cell numbers in Figure 2.

One coating, film III, which was based on polyurethane, showed signs of failure with the formation of blisters; however, the coating appeared intact with no rust, but when removed patches of rust were observed on the metal. In this case no d.c. measurements of resistance could be made with a single cell, but only from cell to cell and this appears to be characteristic of a system where corrosion is taking place underneath the coating. The resistance of the coating had an average value of $10^8 \Omega cm^2$, which is just in the region which Bacon, Smith and Rugg regarded as unreliable.

The frequency response spectrum of this coating was characterized by two relaxation times, representative of two RC networks, although generally one or both of the semicircles represented in the Nyquist plot, Figure 9, was depressed. This general feature appears to be common with other work in which painted specimens show signs of corrosion beneath the coating[4-8].

Discussion

The data presented above demonstrate that the resistance of an intact paint coating measured by a.c. frequency response analysis and by high impedance d.c. voltmeter is the same. The resistance as measured by a.c. is not a function of frequency; neither is it lower than the measured d.c. value as reported earlier[2,3]. This is true both for detached paint films and for attached films. Moreover, the resistance of the attached coating may be determined using cell-to-metal or

Figure 7

Impedance of paint I measured from cell 3 to metal. OV d.c., 0.35V(rms) a.c.

Figure 8

Impedance of paint I measured from cell 2 to cell 3; 0.5V d.c., 0.15V(rms) a.c.
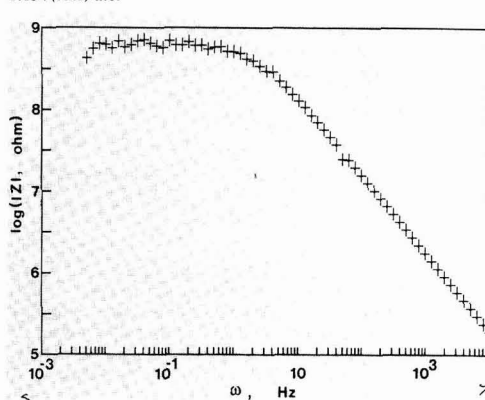

Table 1

D.c. and a.c. resistances (R(d.c.) and R(a.c.)), and capacitances (C) of detached clear epoxy films. The d.c. values are each the mean of two measurements made with the leads reversed.

Coating	Thickness μm	R(d.c.) Ω	V(rms) V	V(d.c.) V	R(a.c.) Ω	C pf
A	60	10^6	0.005	0	2.8×10^6	99
			0.010	0	2.8×10^6	106
B	110	7×10^7	0.100	0	6×10^7	44
			0.100	0.2	3.7×10^7	47
			0.040	0.8	3.5×10^7	44
			0.040	3.0	2.6×10^7	45
			0.040	9.0	2.9×10^7	44
C	115	2×10^8	0.100	0	2.1×10^8	55
			0.100	1.0	1.8×10^8	55
D	70	4×10^{10}	0.200	0	4.5×10^{10}	40
			0.600	0	4.4×10^{10}	43
			1	0	3.2×10^{10}	40
			6	0	4.4×10^{10}	45
			0.600	3	1.7×10^{10}	43
			0.600	6	1.8×10^{10}	50
E	120	4×10^{11}	6.5	0	10^{11}	81*
F	95	6×10^{12}	n			

n - not measured.
* - measured at 1 Hz.
V(rms) is the applied a.c. voltage.
V(d.c.) is the superimposed d.c. voltage.

cell-to-cell measurements, of the type illustrated in Figure 2, the latter method giving the sum of the two appropriate cell-to-metal resistances. The resistances of the coatings described in Figures 3-8 and Tables 1 and 2 are all high ($> 10^8\ \Omega$) and none of the painted specimens, save for specimen III, showed any sign of breakdown or corrosion, before, during or after measurement. Measurements have shown that films with initial resistances of $10^{10}-10^{12}\ \Omega cm^2$ usually fall in resistance by an order of magnitude after some months of immersion. It seems that the limit for reliability of Bacon, Smith and Rugg should be raised from $10^8\ \Omega cm^2$ to $10^9\ \Omega cm^2$.

The maximum amplitude of the applied a.c. voltage under such circumstances is determined purely by the magnitude of the current flowing: this must be sufficiently low that no damage is induced by the perturbation, but high enough to provide measurable current at low frequency. For the present apparatus this is apparently viable at a minimum current of $\sim$ 0.1nA. At 10V peak amplitude the mean electric field impressed across the 100μm thick film is 1000V cm^{-1}. This field is insufficient to cause damage to the films, at least for the present high resistance systems. The a.c. technique was unable to resolve any component of the intact painted metal surface, other than the paint coating itself, although clearly, electron transfer at the metal/paint interface should be considered as a separate component with a distinct RC time constant.

Specimen III, whose frequency response is given in Figure 9, showed visible signs of failure of the paint, with formation of blisters. Since failure of the specimen took place at isolated spots one can view the equivalent RC network as shown in Figure 10a. In this figure it is imagined that the paint coating covers the entire surface with a single resistance; this component is defined as R_F, C_F. Beneath the paint coating lies a number of isolated patches of corrosion, with a local electrolyte beneath the intact paint film within each blister. Each blistered region is defined as R_{Pi}, C_{Pi}, and these are all connected in parallel, but in series with the paint coating. The circuit then resolves into two components with two RC time constants. The fact that there are many corroded areas over the specimen surface, covering a distribution of sizes, and presumably of development, results in apparent depression of one of the semi circles shown in Figure 9.

Table 2

D.c. and a.c. resistances (R(d.c.) and R(a.c.)), and capacitances (C) of paint films supported on mild steel. With the exception of paint no. III each d.c. resistance is the mean of two measurements taken with the leads reversed. For paint III the individual measurements are given.

Paint	Thickness μm	Cell Measurement	R(d.c.) Ω	V(rms) V	V(d.c.) V	R(a.c.) Ω	C pf.
I	68	1	4×10^8	0.35	0	2.9×10^8	241
	62	2	6×10^8	0.35	0	4.6×10^8	133
	60	3	2×10^8	0.35	0	9.5×10^7	398
				0.15	0.2	1.1×10^8	362
				0.15	0.5	7.8×10^7	362
				0.15	1	6.2×10^7	362
		1:2	5×10^8	0.6	0	8.3×10^8	84
		1:3	5×10^8	0.35	0	6.6×10^8	145
		2:3	6×10^8	0.35	0	6.4×10^8	99
II	30	1	3×10^8	0.3	0	1.5×10^8	306
	35	2	3×10^8	0.3	0	3.3×10^8	212
	41	3	3×10^8	n			
		1:2	5×10^8	0.3	0	3.3×10^8	212
				0.3	0.5	5×10^8	133
				0.3	1	4.6×10^8	133
				0.3	2	4.8×10^8	133
				0.3	4	4.9×10^8	133
				0.3	9	3×10^8	133
		1:3	5×10^8	n			
		2:3	6×10^8	n			
IIIm	n	1	n	0.005	0	7.3×10^5	647
		2	n	0.05	0	6.9×10^6	357
		1:2	3×10^8	0.05	0	3.2×10^7	380
		2:1	4×10^7				
		1:3	6×10^8	0.3	0	7.5×10^7	420
		3:1	6×10^7				
		2:3	4×10^8				
		3:2	2×10^8				
IV	270	1	7×10^{12}	n			
	300	2	6×10^{12}	n			
	310	3	10^{12}	n			

I : zinc chromate primer plus green gloss drying oil coat.
II : white gloss drying oil paint.
III : cinnamon-coloured polyurethane paint.
IV : clear epoxy lacquer.
n - not measured.
m - The frequency response of this coating showed more than one component (see Figure 9) and the metal showed evidence of corrosion beneath blisters in the paint. The a.c. parameters presented are those ascribed to the paint coating alone.
V(rms) is the applied a.c. voltage.
V(d.c.) is the superimposed d.c. voltage.

Figure 9

Impedance of paint III measured from cell 1 to cell 3. OV d.c., 0.3V(rms) a.c.
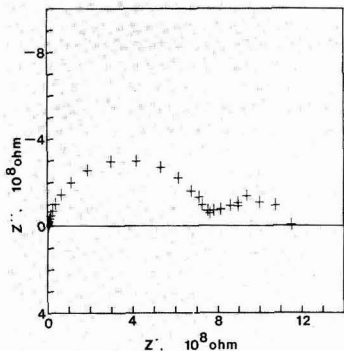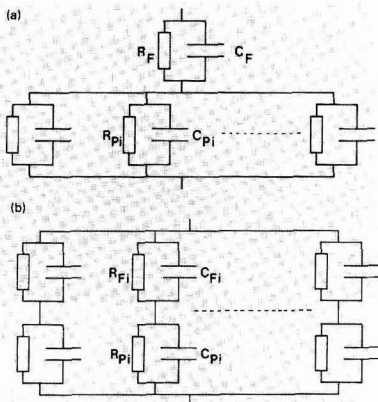

Figure 10

Possible equivalent circuits describing the impedance of paint III. (a) Corrosion beneath isolated blisters is covered by a paint coating of constant impedance characteristics, (b) The impedance characteristics of the paint coating covering each corrosion blister is unique to that blister.

One may alternatively view the equivalent circuit as shown in Figure 10b. Here, each metal/electrolyte/paint blister system is a separate component, with R_{Pi}, C_{Pi} describing the corrosion process beneath the blister, and R_{Fi}, C_{Fi} describing the properties of the paint overlying the blister. The difference between Figures 10b and 10a is the assumption in Figure 10b that the paint overlying the blisters has undergone a significant reduction in resistance during development of corrosion and thereby effectively shorts out the higher resistance of the paint overlying uncorroded areas of the specimen. Again because of the number of blisters, an apparent depression of the semicircles shown in Figure 9 is anticipated. For the present data both equivalent circuits are equally suited.

One may use the magnitude of the capacitance to determine which of the two components shown in Figure 9 is associated with the paint coating. The first component gives a capacitance of 271 pf; the second component gives a capacitance of ~ 0.2 μF (measured at 45 mHz). Comparison of these values with those given for other paint coatings in Tables 1 and 2 shows the former to be that associated with the paint coating and the latter with the corrosion process beneath the paint.

Conclusions

1. In the absence of corrosion the resistances of paint films measured by a.c. and d.c. techniques are the same and no polarisation resistance is detected.

2. The amplitude of the perturbing voltage used to measure the a.c. impedance of paint coatings is determined purely by the magnitude of the current response. The more resistive the coating, the higher the amplitude which can be applied without causing significant damage.

3. Cell-to-cell measurement of the impedance provides a suitable method for measurement of the a.c. impedance and eliminates the need for knowledge of the open circuit potential and its variation with time.

4. For a painted metal in which corrosion is occurring beneath blisters in the paint the equivalent circuit is resolvable into two overall RC networks with dispersion of the time constants arising from variation in the size and degree of development of the blisters.

5. The a.c. method allows resolution of the individual components of the system and provides a means of detecting corrosion beneath the coating.

Acknowledgements

References

1. Bacon, R. C., Smith, J. J. and Rugg, F. M., *Ind Eng. Chem.*, 1948, **40**, 161.
2. Buller, M., Mayne, J. E. O. and Mills, D. J., *JOCCA*, 1976, **59**, 351.
3. Buller, M., Ph.D. Thesis, University Library, Cambridge, 1976.
4. Callow, L. M. and Scantlebury, J. D., *JOCCA*, 1981, **64**, 83.
5. Callow, L. M. and Scantlebury, J. D., *JOCCA*, 1981, **64**, 119.
6. Callow, L. M. and Scantlebury, J. D., *JOCCA*, 1981, **64**, 140.
7. Callow, L. M. and Scantlebury, J. D., *JOCCA*, 1982, **65**, 11.
8. Callow, L. M. and Scantlebury, J. D., *JOCCA*, 1983, **66**, 93. ∎

Fireproofing of offshore structures with epoxy intumescent materials

by J. V. Dunk, Avco Speciality Materials, 7b Ongar Rd, Brentwood, Essex CM15 9AU, UK

Introduction

Since the earliest days of offshore exploration and production, there has been a requirement to fire protect steel structures and firewalls against the effect of hydrocarbon fire. In the early days materials were used which were derived from fire protection of structural steel in buildings and, to a certain extent, structural elements of onshore petroleum and petrochemical installations. Over the years, the shortcomings of traditional materials used in this fashion became very evident particularly in the North Sea environment. Cementitious products with very limited physical strength and flexibility are easily damaged during the normal operation of a platform and also during loadout and installation of modules during construction. Additionally, all water-based and cementitious materials rely on a weatherproof topcoat to retain their fire integrity and that of the substrate steelwork against corrosion. The cost of maintaining these materials offshore has never been fully documented but on some major Norwegian platforms it is known that maintenance costs run into some hundreds of thousands of pounds per year.

As well as durability of product, there are a number of other factors which are very relevant to the selection and use of material for fire protection offshore. Some of the major considerations are:
☐ Installed weight
☐ Toughness and durability
☐ Maintenance requirement
☐ Ease of application
☐ Prevention of corrosion underneath the fire protection material.

Another factor to become more evident in recent years has been the dimensions of the fireproofing material. As platforms are designed to be lighter in weight, structural dimensions are reduced and the congestion in modules for services and utilities becomes more evident. The thickness of the fire protection material surrounding structural members, therefore, can be of significant consequence when designing to prevent the clash of pipework and other utilities with structural elements.

Probably one of the most important factors to be considered when reviewing passive fire protection materials is the additional weight that will be added to the structure. Durability and low maintenance are requirements for fire protection materials which have come to the fore in only the most recent years as operators recognise the significant costs involved in ensuring that their fire protection remains in serviceable condition, i.e. it will provide the designed fire protection should the fire incident happen. On many projects, however, there still remains considerable differences of opinion between those building the platform who are interested in capital expenditure costs and those operating the platform whose maintenance budget will pay for fire protection maintenance.

Epoxy intumescent fire protection materials

Intumescent materials provide thermal insulation to the substrate by reacting to the fire's heat and creating an insulating blanket of char which, as well as insulation, re-radiates the fire's heat back to the fire itself. It is this thermal blockage which contributes significantly to the ability of a thin film coating to provide significant levels of fire protection at low applied weight. Intumescent materials vary greatly in their intumescent action. They can be formulated to expand many hundreds of times original material thickness with resultant very weak char, or to a few times the original thickness with a much tougher and stable char which is able to withstand not only the thermal draught of a fire situation but also active water protection systems without removal or detriment to the char itself. Our own particular products, Chartek 59 and Chartek III, have been formulated to provide protection of the latter type.

Intumescent fire active ingredients can be introduced into a number of mediums including solvent, emulsion and epoxy bases. As a manufacturer of epoxy intumescent coatings for 14 years and with the same period of real time experience in the field, we are confident that experience has shown epoxy systems to be the best carriers for intumescent products, particularly when used in external locations and harsh internal locations such as wellhead and processing modules on offshore structures.

What are the advantages of epoxy intumescent materials?

There are a number of advantages of epoxy intumescent products for offshore fire protection, the following are some of the most significant:

Weatherability. Epoxy materials are well known for excellent weatherability without degradation, even in severe marine environments. Encapsulating fire active ingredients in an epoxy medium results in a product which is inherently weatherable and will not degrade in terms of its fire performance due to exposure to the elements. Our own products have been thoroughly tested by the American Underwriters Laboratories for their exterior listing programme. This programme evaluates the reliability of a material in terms of its fire performance after exposure to accelerated ageing and weathering. Both Chartek 59 and Chartek III products have passed Underwriters Laboratories' programme *without* a topcoat.

Durability. Epoxy intumescent products have outstanding resistance to mechanical damage both in terms of impact and abrasion resistance. Despite having a compressive strength several times in excess of that of dense concrete, Chartek III also remains a material which is more flexible than the substrate steel itself. Therefore, under-flexing during loadout of modules or in operation, the material does not crack and debond from the substrate.

Maintenance. Epoxy intumescent products are essentially maintenance free because of their built-in weatherability. Whilst topcoats are often used on these products for colour purposes and to enhance their weatherability, the integrity of the material is not deteriorated should the topcoat be lost. Maintenance of the topcoat therefore can take place as and when desired, whereas topcoat maintenance with cementitious and water-based products is crucial to the integrity of those materials.

Corrosion protection. Epoxy paints are known to provide

outstanding corrosion protection and are often used at thicknesses of approximately one third of a millimetre to provide total corrosion protection for offshore structures. Epoxy intumescent materials are applied at thicknesses generally in excess of 5mm and provide corrosion protection as an additional benefit to fireproofing in the one coating. A significant concern with other fire protection mediums is the potential of corrosion taking place to the substrate steel, and mesh reinforcement which holds the material to the steel in the event of a fire, which is undetectable from the surface viewpoint.

Application procedures. Application of any passive fireproofing is viewed with some dissension by most construction yards because of the necessity to keep the application area clear during application of product. The environmental requirements for all passive fire protection materials used offshore differ very little. One advantage of epoxy intumescent materials is their ability to cure to full hardness within 24-48 hours in comparison with up to 14 days for water-based and cementitious materials.

What are the disadvantages of epoxy intumescent materials?

Whilst the advantages significantly outweigh the disadvantages of epoxy intumescent materials, there are some points to note:

Smoke and fume generation. Epoxy materials are organic and therefore in a fire situation will liberate a certain level of smoke and fumes. The fumes given off by epoxy materials generally are carbon dioxide and carbon monoxide, as well as some other trace gases. In the past, the fact that a fireproofing material gives off smoke and toxic fumes, and has limited combustibility, has been viewed in a very emotive way. The reality is that the materials (at least those produced by Textron) only begin to liberate smoke and fumes at elevated temperatures, in excess of 300°C, in direct exposure to the fire. In comparison with the smoke and fumes given off by an oil or gas fire, the quantity and toxicity of smoke and fumes given off by the epoxy intumescent material is not significant. The material is therefore not contributing any significant additional hazard to the fire situation itself. The question of smoke and fume generation has been addressed by operators, petroleum authorities and certifying authorities. Whilst intumescent products would generally be excluded from use in such internal areas as accommodation modules, control rooms and safe havens, the use of the products in all other areas of the platform, both internal and external, generally receives little comment from the authorities.

Cost. The installed cost of an epoxy fire protection material can be a factor of two or three times that of cementitious products. Therefore, on initial review, they can be the least favoured product. What has to be decided, however, is the difference in terms of installed cost and the maintenance requirements offshore. With maintenance of topcoats offshore costing as much as £35 per square metre once all costs have been taken into account, plus the extremely high cost of replacing failed materials, the initial higher installed cost of epoxy products can be readily justified. One major offshore operator showed in review of candidate materials for a new development that the cost of one application of topcoat to a cementitious product on a module support frame offshore outweighed the difference in cost between epoxy intumescent and cementitious material during a construction phase.

The right material for the right location

To a certain extent epoxy intumescent materials are "install and forget" products, however their use generally requires justification of the additional cost and, to this end, the primary locations for the product on offshore structures are:
☐ External structural steelwork and bulkheads
☐ Structural steelwork and bulkheads in open process modules
☐ Underdeck applications
☐ Use in modules where mechanical damage and vibration are a problem (e.g. wellhead and process)
In other areas of the platform where installation is in an internal controlled environment location without mechanical damage potential lower grade materials make more economic sense, particularly if access can easily be gained for any potential maintenance requirements. It is therefore up to the designer and operator to address these questions at an early stage of design and to consult with the manufacturers for information relative to their specific products.

Explosion resistance

The scenario of explosion before fire on an offshore platform and the effect of the explosion pressure wave on the passive fire protection material applied to structural steel and firewalls in the area is a matter of much discussion at this time, particularly in Norway. It is evident that an expolsion followed by hydrocarbon fire is one of the most dangerous hazards to present itself during the operation of an offshore installation. The ability of the passive fireproofing material to remain undamaged and soundly attached to the steel substrate after explosion has been addressed by actual and simulated explosion testing on both structural elements and firewalls by a major Norwegian scientific institute.

The pressure wave from an explosion causes deformation reverberation in the steelwork with the passive fireproofing material being subjected to both compressive and tensile load. Comparative explosion and subsequent fire tests conducted on vermiculite cement, magnesium oxychloride cement and epoxy intumescent materials have shown that the latter, by virtue of their superior adhesion and mechanical strengths, have significantly better performance in an explosion situation than the cementitious products. Epoxy materials will remain effective while steel substrates deform well into the plastic region.

The use of wire mesh reinforcement

Textron continue to strongly advocate the use of wire mesh reinforcement, even with epoxy intumescent materials despite the exceptionally high adhesion of these products to the steel substrate. There are two main reasons for the use of wire mesh reinforcement. The first is the ultimate adhesion to the fireproofing material in the fire situation. Despite having adhesion in excess of 6Mpa Chartek, and other spray applied intumescent materials, are normally applied to the substrate over organic primer systems. The majority of organic primers rapidly lose their adhesion and cohesion at elevated temperatures, around the 200-250°C level. When protecting steelwork to a temperature of 400°C or possibly 550°C, it is quite probable to assume that the interface between the fire protection material and the steel will reach the temperature of 200-250°C quite legitimately during the period of the fire. Therefore, it is evident that with a weakened primer system due to the higher temperature, the majority of adhesion that

Satisfying the safety regulations

by A. J. Hinton, Hinton Safety Consultants, 2a Myrtle Grove, Whitefield, Manchester M25 7RR, UK

Profitable research and development requires investing time and effort (i.e. money) in developing ideas which will be successful in a future market. In particular, the successful marketing of a new substance or formulation often depends on applications research to ensure that it is presented in the appropriate form to meet the intended market requirements in terms of technical effect and cost/efficiency.

Product developers must now consider, at an early stage, the additional cost factors of health and safety when estimating product viability; previously, these have been relatively minor costs compared to the costs of research staff and overheads, but the increasing volume and complexity of national and international health and safety regulations means that the "regulatory clearance" costs are now a substantial part of the development budget.

These extra costs for new product development (Table 1) arise in a number of ways from several pieces of legislation, mainly originating from EEC Directives.

The largest, and calculable, add-on costs arise from the need to carry out a mandatory set of tests to satisfy the EEC notification requirements of directive 79/831/EEC[1] the 6th Amendment to the so-called Substances Directive 67/548/EEC[2];

Another cost factor arises from the delay which these tests add to the date when marketing can commence, e.g. between 9 and 15 months, depending on various factors, such as the route of exposure and the need to carry out tests additional to those in the Base-set.

A third cost factor, which concerns all new preparations of both new or existing substances, is the need under the new Dangerous Preparations Directive 88/379/EEC[3] to assess, package and label all preparations according to the instructions of this Directive.

Finally, a difficult-to-calculate cost factor is the effect of recent legislation on product liability[4,5]. This affects all products for up to 10 years after marketing. Obviously, potentially high risk (see Equation 1) products could affect insurance cover rates in addition to costs of providing practical and adequate information to enable safe manufacture, packaging, transportion and handling.

$$RISK = f_1(EXPOSURE) \times f_2(HAZARD) \qquad (1)$$

Since the cost of regulatory clearance testing for *new substances* takes no account of the selling price of the substance, products which sell in small quantities at high prices have relatively lower clearance costs than large volume, low priced commodity chemicals. This is demonstrated in Table 2.

The Base-set testing requirements are valid for substances which sell for up to 10 tpa, and possibly up to 100 tpa if the tests show little potential toxicity or ecotoxicological problems.

Level 1 tests are triggered when the selling rate exceeds 100 tpa (500 tonnes total), or at the lower level of 10 tpa (100 tonnes total) if problems arise from the Base-set results.

Level 2 tests are required when the marketed rate exceeds 1000 tpa (5000 tonnes total). Thus over a million pounds sterling could be spent in testing costs for a product which sells at the rate of over 1000 tonnes per annum in the EEC, adding a potential £1,000 per tonne cost to the first years' sales.

However, there is no legal requirement to do any tests

Table 1
Effects of legislation leading to additional development costs

Added-On Development Costs
Plus . . . . . Notification Tests (e.g. EEC, USA, Japan etc)
Plus . . . . . Delay in Marketing (e.g. 9 to 15 months)
Plus . . . . . Costs of Complying with Dangerous Preparations Directive
Plus . . . . . Liability Costs (e.g. EEC Product Liability Directive, UK Consumer Protection Act etc)

Table 2
Estimated costs of notifying a new substance in the EEC, at various tonnage levels

Notifying New Substances in EEC			
Level	Tonnage Per An	in EEC Total	Approx Cost £
Base-set	<10 (<100)	<50 (<500)	30,000- 70,000
Level 1	≥100 (≥10)	≥500 (≥50)	70,000- 180,000
Level 2	≥1000	≥5000	500,000- 1,000,000

Table 3
Summary of EEC notification requirements

New Product Development
EINECS —— listed → market
not listed ↓
Must Notify (79/831/EEC)
Items: Identity
Tonnages
Uses
Physico-chemistry
Toxicology
Ecotoxicology
User label
Disposal
Costs: £30,000 - 70,000
Base set
£70,000 - 1 million
Level 1/2
Delay: 9 to 15 months (or more)

additional to those of the Base-set — the procedure is to inform the Competent Authority when the tonnage levels are reached, when the C. A. will then start a dialogue on the further tests required to be done; this may, of course, be immediately after acceptance of the Base-set dossier.

How do you know if it is "notifiable"? Check in the EINECS inventory; if it's listed, it's not notifiable. Otherwise it is notifiable (Table 3). Some problems exist with polymers and these have not yet been resolved — clearly the 6th Amendment[1] requires polymers containing more than 2% of a *new monomer* to be notified. One problem arises because there could be an infinity of new polymers from any new

Table 4

A comparison of the requirements of EEC, USA, and Japanese new substance notification regulations

1. Regulation		EEC 'Sixth Amendment' (Directive 79/831/EEC) Annex VII; Base Set	USA 'Premanufacture' Notification for New Chemical Substances (TSCA, Section 5)	Japan 'Chemical Control Law' as amended 1986
2. Nature of sample to be tested		Technical substance as produced by industry	Substance as manufactured	Purity 90% for all tests except toxicology
3. Identity—	IUPAC and other names	●	●(or CAS)	●
	Empirical and structural formulae	●	●	●
	Purity	●	●	●
	Nature of impurities and %	●	●	●
	Other Additives	●	●	●
	Spectra	● (UV, IR and NMR)		
	Detection and determination methods	●		
	Process description		●	
4. Information—	Proposed uses	●	●	●
	Fields of application; open/closed systems	●	●	●
	Production for each use	●	●	●
	Number of workers involved -controlled by Notifier		●	
	-conrolled by Others		●	
	Recommended methods-storage handling, transport, fire, others	●		
	Emergency measures-spillage injury to persons	●		
5. Physical Chemistry—	m.p./b.p	●	)	●
	Relative denisty	●	)	
	Vapour pressure	●	)	
	Surface tension	●	)	
	Water solubility	●	)	●
	Fat solubility	●	)	●
	Solvent solubilities- ethanol, hexane, toluene		)See Note 1	●
	acetone, n-octanol and chloroform		)	
	Partition Coefficient (in-octanol/water)	●	)	●
	Flash Point	●	)	
	Flammability	●	)	
	Autoflammability	●	)	
	Oxidisability	●	)	
6. Toxicology—	Acute toxicity	● (2 routes)	)	
	Skin irritation	●	)	
	Eye irritation	●	)see Note 1	
	Skin sensitisation	●	)	
	Sub-acute toxicity (28 days)	●	)	●
	Mutagenicity-Ames	●	)	●
	-other	●(non-bacteriological)	)	●(In-vitro cytogenetics)
7. Ecotoxicity—	Acute toxicity fish	●	)	●(special protocol)
	Acute toxicity Daphnia	●	)See Note 1	
	Biodegradability	●(Min. BOD/COD ratio)	)	●(If biodegradable by special protocol)
	Abiotic degradation	●	)	
	Fish accumulation (if not biodegradable)		)	● (if LogPo/w≥3, by special protocol)
8. Possibility of rendering the substance harmless-recovery/neutralisation/destruction, etc.		●	See Note 1	
9 Estimated cost for data package (Note 2)		£30,000-£70,000	£5,000+	£16,000-£30,000

● = Mandatory, using agreed protocols (Annex V of Directive 79-831/EEC for EEC. OECD accepted by Japan and USA except where otherwise stated)

Note 1 — notifier must submit all test data as full reports in his possession or control and indicate what may be available but not under his control; EPA must decide on basis of available information whether the substance 'may present an unreasonable risk' to man; EPA may use SAR to estimate these risks in absence of other data.

Note 2 — includes administration costs of Notifier — higher figure is appropriate if (i) expensive routes (e.g. inhalation) are necessary, (ii) limit tests cannot be used, (iii) additional expertise or work is necessary to resolve interpretations, (iv) new specific analytical techniques need to be devised, and, in the case of Japanese law, either the fish accumulation or the biodegradability tests are required.

monomer; the UK industry position, agreed with the CIA, is based on fully testing the extreme ends of the polymer which contains more than 2% of the new monomer and notifying these with a full Base-set — the remaining "in-between" polymers should also be notified, but using analogy rather than toxicological and ecotoxicological test results, supported by physico-chemical data, to arrive at hazards. The monomer only needs to be notified if it is being marketed in its own right.

The European Commission is holding meetings of Competent Authorities to try to resolve the whole matter. Some authorities are trying to raise the whole question of what is a polymer and if this line is adopted, it could lead to considerable complications, particularly with respect to what was not allowed to be listed in the EINECS Inventory! The author can only recommend that one follows the UK industry attitude.

If it is notifiable, then information must be supplied on a number of aspects of the substance, some of which encroach on areas of commercial confidentiality (e.g. exact structure, impurities, etc)[6].

The delay time is composed mainly of the time to conduct the longest study, the 28-day exposure study, which may take 3-4 months to prepare, conduct and report. However, this cannot start until an adequate supply of representative material is available, until space has been booked at a testing facility and until other acute tests have been completed; at the present time, because of the pressure of work created by the new regulations on industrial and agricultural chemicals, it may be 3 months before some laboratories can start tests and 6 to 9 months before the final reports are made available for the Notification dossier. After this, allow 60 days for acceptance by the Competent Authority (i.e. 2 weeks checking the data before the 'clock starts' on the 45 day mandatory period) before marketing can commence. All this adds up to a minimum delay of 9 months, which can spread into 15 months or more before the new substance or formulations containing it can be marketed in the EEC.

Obviously, it makes sense to consider potential hazard problems which the new substance may exhibit, for example by considering structure relationships with other, similar products and perhaps by carrying out screening tests on the most likely candidate substances for the most critical property (e.g. mutagenicity, acute toxicity, skin sensitisation, etc.), before embarking on the full Base-set tests. Consultants in this area can advise.

This, then, is a very brief summary of what has to be considered when developing a new substance in the EEC. Similar, but generally less stringent or costly, procedures operate before new substances can be marketed in the USA, Japan, Australia, Canada, Scandinavia, Austria or Switzerland[7] (Table 4).

But a lot of innovation occurs through formulating existing substances into new products for specialised applications, e.g. compatibility with paints, emulsions, solvents, water etc., stability under specific storage, weather conditions etc (North Sea oil). The latest all-embracing regulation which lays down the procedure for assessing the safety of such products is the Dangerous Preparations Directive, Council Directive 88/379/EEC. (Table 5) highlights its main areas.

After much consultation and deliberation over many years, the Council Directive on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of *dangerous preparations* was adopted on 7 June 1988 [3]. It must be enforced by Member States by *not later than 7 June 1991*.

The most important aspect of this Directive as far as the paint industry is concerned is that it repeals the Solvents Directive[8] and the Paints, etc. Directive[9]. However, by way of derogation, preparations classified, labelled and packaged according to this earlier directive may be marketed until one year after the new Directive comes into force — this means not later than 7 June 1992, or possibly earlier in those States where the Directive is enacted before 7 June 1991. It is unlkely to be enacted before this date in the UK, since it still has to go through the stages of Consultative document leading to discussions with industry, and amendment or repeal of the UK-CPL Regulations[10].

Since this is likely to be one of the most important pieces of EEC legislation to affect everyone who markets chemical products in the EEC, a fairly extensive summary is given:

1. Whereas the so-called Substances Directive [2] and its various amendments deals with the classification, packaging and labelling of substances, this new Directive covers preparation, i.e. mixtures of two or more substances.

2. Excluded from consideration are Medicines; Veterinary products; Cosmetics; Waste; Pesticides (for at least two years) — where they are subject to other EEC Directives — Munitions; and human and animal foodstuffs in the form "intended for the final consumer".

3. The so-called Solvents Directive[8] and Paints, etc, Directive[9] have been repealed, but, by way of derogation, preparations classified, packaged and labelled according to these earlier Directives may be marketed until one year after the new Directive "comes into force", i.e. until not later than 7 June 1992.

4. Member States must report on the "inadequacies or loopholes" in the so-called Pesticides Directive[11] within two years of application of this Directive, at which time, the commissioners "will, if appropriate, submit the necessary proposals".

5. Member States must enforce the new Directive not later than 7 June 1991.

Table 5

Summary of requirements of the Dangerous Preparations Directive

Dangerous Preparations Directive 88/379/EEC
Applies to all preparations (except Medicines, etc)
Repeals Solvents, Paints, etc., Directives
Phys-Chem Props must be determined (Annex V Methods), <u>unless</u> no explosive, oxidising of flammables present <u>and</u> "unlikely to present such dangers"
Health Hazards "conventional method", or testing (Annex V Methods)
Similar Preps do not need reassessment provided only small changes in dangerous constituents and <u>no</u> new constituents
Authorities may request composition information and question label warnings
Enforceable Before 7 June 1991

6. The physico-chemical properties of the preparation must be determined by testing using Annex V methods; the only basis for not testing appears to be if the preparation does not contain any explosive, oxidising or flammable substances and "on the basis of information available to the manufacturer" is unlikely to present dangers of this kind.

7. The health hazards must be determined by a "conventional method" (explained below) or by testing using Annex V methods of Directive 67/548/EEC[2]. If both methods are used, the results of testing take precedence, in general (Article 3.3). Other points are:

(a) Similar preparations do not need to be re-assessed provided that no constituents have been substituted and that changes in the composition of the dangerous constituents do not exceed 0.25-2.5% by weight of the composition (the actual figure depending on the concentration in the original tested preparation) (Article 3.4).

(b) The conventional method uses the concentration limits

given in Annex I to the Substances Directive [2] when the substance is listed there; otherwise (and this refers to the majority of substances and, therefore, preparations) concentration limits must be assigned to each component substance by a method described in Annex I to the new Directive (Article 3, and Annex I). For example, a preparation containing more than 7% of a substance classified as "very toxic" which carried any of the risk Phrases R26, R27, R28 would be itself classified as "very toxic" and would carry the same R phrases; if it contained between 1% and 7%, it would be classified as "toxic" and the R phrase (R23, R24 or R25) appropriate to the route would be used; if it contained between 0.1% and 1%, it would be "harmful"; and if it had less than 0.1% it would not be classified as dangerous.

(c) Preparations which contain substances being notified under 79/831/EEC[1], and hence labelled "Caution — substance not yet fully tested", must carry a label "Caution — this preparation contains a substance not yet fully tested", in addition to any other warnings arising from any known hazards of the preparation (Article 3.5).

(d) (Article 3.6) Unless otherwise specified in the Annex I to 67/548/EEC[2], no account needs to be taken of impurities or additives if they are:

☐ Toxic or very toxic, present at < 0.1%.

☐ Harmful, corrosive or irritant, present at < 1%.

(e) Preparations containing known respiratory or skin sensitisers at 1%, or higher, levels must carry the appropriate warnings and risk phrases (Harmful, R42 for respiratory; Irritant, R43, for skin) and must carry the name of the sensitiser on the label (Article 7(c)(ii) and Annex 1, Table V).

8. Member States may request information from the manufacturer on the composition and "any other pertinent information", if they have information to doubt compliance with this directive (Article 5). Therefore, this requires that the manufacturer should hold information on the classification and labelling of his preparations "at the disposal of the authorities of the Member States".

9. Requirements for tactile warnings and child-resistant fastenings apply to certain categories of dangerous chemicals, yet to be defined. Containers sold to the general public must not be of a shape or type to arouse the "active interest of children or to mislead customers" or be confused with foodstuffs, cosmetics or medicines (Article 6).

10. In brief, the information on the label must clearly show (Article 7):

(a) The trade name.

(b) the name/address-telephone number of person responsible for placing it on the market in the EEC.

(c) If the preparation is classified as Very Toxic, Toxic, Harmful or Corrosive, the chemical names of the Very Toxic, Toxic, Harmful and Corrosive (R35) or (R34) substances must be mentioned if present at > of =0.1%, 3%, 25%, 1% (R35) or 5% (R34), respectively.

(d) Four names are considered sufficient, but preparations which are mutagenic, carcinogenic, teratogenic, sensitising, or produce irreversible effects (R39, 40) or serious damage on prolonged exposure (R48) must name the substances involved; i.e. the names of these substances take priority, presumably even if they are not responsible for the major dangers of the preparation.

(e) The symbols of danger, with the following priorities:
Toxic, makes Corrosive and Harmful optional
Corrosive, makes Harmful optional
(Harmful, makes Irritant optional)
Explosive, makes Flammable and Oxidisable optional

(f) The appropriate Risk and Safety phrases for all the principal dangers of the preparation — a maximum of four of each should normally be sufficient.

(g) Any special provisions in Annex II relating to preparations sold to the general public, preparations containing lead, or cyanoacrylates, or isocyanates or epoxy resins, or preparations used for spraying.

11. The size of the label, the dimension(s) of the symbol(s) and the colour and presentation are given in Article 8 — this follows the same lines as the labelling of substances.

12. This Directive also contains a provision requiring Member States to take "the measures necessary to implement a system of specific information (in safety-data sheet form) relating to dangerous preparations" . . . within three years of the adoption of this Directive, i.e. by 7 June 1991.

The final area which is briefly mentioned is the Product Liability Directive[4], which came into force in the UK in March 1988 in the form of the Consumer Protection Act (Table 6).

This regulation makes the supplier — and this means anyone in the chain of supply to the user — responsible for any defect which leads to damage to property or person, for up to ten years after marketing.

Table 6
Summary of product liability requirements

Consumer Protection Act 1987 (Incorporating Product Liability Directive 85-374-EEC)
Supplier (any in the chain) responsible for any Defect, which leads to damage to person or property, for up to 10 years after marketing.
A Defect exists if safety is not what one would be entitled to expect, taking account of manner of marketing, warnings given, time it was supplied and purpose to which product might be expected reasonably to be put.
("Development risks" defence — in UK, can argue that defect could not have been foreseen by those familiar with the art)

A "Defect" is considered to exist if safety is not what one would be entitled to expect, taking into account the manner of the marketing, the warnings given, the time it was supplied and the purpose to which the product might be expected reasonably to be put.

In the UK Act there exists what is called a "development risks" defence, i.e. it is a defence, if it can be argued that the defect could not have been foreseen by those familiar with the art at the time it was marketed. However, this defence is unlikely to carry any weight in Europe since it is a bone of contention with some other Member States.

A substance or preparation with high human or environmental hazards risks represents not only the possibility of a higher insurance premium but also requires higher financial investment in terms of engineering controls, worker protection and training for its safe manufacture and for its safe packaging, storage, transport and use by customers.

This then summarises the major new factors which affect the planning of new chemical products and which must be considered at various stages during the development of a new substance or preparation. For his own and others health and safety and for the success of the products which he develops, the Research Chemist can no longer work in isolation and remain ignorant of these external factors.

References

1. Council Directive 79/831/EEC, O. J. L259 (Oct. 1979) 10.
2. Council Directive 67/548/EEC, O. J. 196 (Aug. 1967) 1.
3. Council Directive 88/379/EEC, O. J. L187 (Jul. 1988) 14.
4. Council Directive 85/374/EEC, O. J. L210 (Aug. 1985) 29.
5. Consumer Protection Act 1987, HMSO.

6. A. J. Hinton, JSDC, 1986, 102, 1.
7. A. J. Hinton, Rev. Prog. in Colouration, SDC, 1988, 18.
8. Council Directive 73/177/EEC, O. J. 189 (Jul. 1973) 7.
9. Council Directive 77/728/EEC, O. J. L303 (Nov. 1977) 23.
10. The Classification, Packaging and Labelling of Dangerous Substances Regulations 1984, S. I. No. 1244, HMSO.
11. Council Directive 78/631/EEC, O. J. L206 (Jul. 1978) 13.

Addendum

The first part of my paper deals with the requirements, and the consequential problems, involved in notifying new substances, particularly in the EEC. I have also mentioned the Product Liability Directive and the latest, and all-important Directive (the so-called Dangerous Preparations Directive), dealing with how preparations (as opposed to substances) must be assessed and classified for hazards, and labelled and packaged accordingly. This affects everyone who sells chemicals in the EEC, and must be enforced by 7 June 1991, at the latest.

The future — Proposed changes

Nothing stands still for long in this area and there are several new published proposed Directives covering worker safety and health currently under consideration by European Parliament and the Economic and Social Committee.

However, it is worthwhile spending a few moments considering the proposed changes to new substance notification requirements, which are likely to be published shortly as the proposed 7th amendment to the so-called Substances Directive — you will remember that the 6th amendment laid down the current notification procedures in 1979. Since then, experience has revealed problems in some areas, mainly owing to lack of harmonisation in the interpretation of the regulations by different Member States. The 7th amendment aims at more harmonisation, but not without extra cost to the chemical innovators and not in all the areas of problem to them.

The following tables compare briefly the main changes which are proposed in the draft 7th amendment:

Table 7 — Currently, exports of new substances are exempt from notification requirements and the proposal to require

Table 7

Comparison of 6th Amendment and proposed 7th Amendment

6TH AMENDMENT	PROPOSED 7TH AMENDMENT
EXPORT — Exempt	MUST be Notified
IDENTITY	NO CHANGE
INFORMATION	PLUS — Production process data
	Exposure (Production)
	User process
	Exposure (Users)
	Form/Conc'n as marketed
	Packaging
PHYS — CHEM	LESS — Surface tension
	PLUS — Flam reaction with water
	Pyrophoric properties
TOXICOLOGY	PLUS — Teratology pre-screen
ECOTOXICITY	PLUS — Algal inhibition
	Hydrolysis and photodegn (if not biodeg)
	Adsorption/desorption
OTHERS	PLUS — Safety Data Sheet

them to be notified raises a considerable bone of contention with industry; the feeling is that this is an unnecessary interference with trade. The proposals require the notifier to give information on his customers processes and exposure; how can the seller be expected to know this?

A new teratology pre-screen is proposed, but, even assuming its need at Base-set level, how can it be conducted when no test methods have yet been agreed? The proposals include the requirement to provide a safety data sheet with Base-set notification.

Table 8 — The proposals require that the new substance cannot be marketed earlier than 60 days "after receipt of the notification by the Authority". The present regulations require the dossier to be submitted "at the latest 45 days before the substance is placed on the market . . . ". Since some authorities take a considerable time to decide that the information is complete, before actually starting the "45 day clock", the new proposals are likely to encourage even greater delays! The proposal to label all existing substances which have not been tested to Base-set requirements (i.e. the majority) with "Provisional label" is strongly opposed as negative and unhelpful.

Table 8

Comparison of 6th Amendment and proposed 7th Amendment

MARKETING DELAY

6TH AMENDMENT
"To submit . . . to the C.A. . . . at the latest 45 DAYS BEFORE the Substance is placed on the market . . ."
PROPOSED 7TH AMENDMENT
"Not earlier than 60 DAYS AFTER the date of receipt of the Notification by the Authority"

EXISTING SUBSTANCES
PROPOSED 7TH AMENDMENT
Until fully tested, to be labelled "Provisional label"

Table 9 — In return for supplying a considerable amount of mandatory information, the procedure for Limited Announcements of less then 1 tonne/annum is improved by having to notify only in the country of manufacture, or (for non-EEC manufacturers) where the importing agent is established. At present, information must be presented separately, and in different amounts, to each Member State where marketing takes place. At present, no delay time is specified, but it can be very considerable; the new proposals specify that marketing can commence 15 days after receipt of the information by the Authority, "subject to any conditions which may subsequently be imposed by the authority — it is to be hoped that htis sentence is not interpreted with the same liberality used by some authorities to interpret the sentence "and complies with any conditions imposed by those authorities", which is the main cause of delays and disharmony under the present regulations.

Table 9

Comparison of 6th Amendment and proposed 7th Amendment

"LIMITED ANNOUNCEMENTS"
I.E. REDUCED LEVEL NOTIFICATIONS

6TH AMENDMENT
LESS THAN 1 TONNE/YEAR RATE
"Identity, Labelling data and Quantity and "Any conditions imposed by" the Authorities — In EACH Member State where marketed.
MARKETING DELAY — UNCERTAIN?

PROPOSED 7TH AMENDMENT
LESS THAN 1 TONNE/YEAR RATE
Identity, information on the Substance (35 items), PLUS M.Pt, B.Pt, Water sol., Po/w, Flash Point, Flammability, Acute Toxicity. Skin and Eye Irritation, Skin sensitisation, Ames and Biotic degradation — To THE Member State where manufactured, or where importing Notifier is established.
MARKETING DELAY — 15 DAYS

Table 10 — The proposals for R&D Limited Announcement of more than 1 tonne for one year only have not been harmonised and must continue to be made to each Member State where the product is offered. The acceptance time proposed is 15 days.

Table 10

Comparison of 6th Amendment and proposed 7th Amendment

"LIMITED ANNOUNCEMENTS" CONTINUED I.E. REDUCED LEVEL NOTIFICATIONS
6TH AMENDMENT

MORE THAN 1 TONNE IN 1 YEAR —
"RESEARCH & DEVELOPMENT STAGE"
"Identity, Labelling data and Quantity"; Assurance that only customers' staff using under controlled conditions and "Any conditions imposed by" the Authorities — In EACH Member State where marketed.
MARKETING DELAY — UNCERTAIN??

PROPOSED 7TH AMENDMENT
  MORE THAN 1 TONNE IN 1 YEAR
"PROCESS ORIENTATED R&D."
As for 6th Amendment, PLUS Justification for Research, List of customers — In EACH Member State where marketed.
MARKETING DELAY — 15 DAYS

Table 11 — A new category of Limited Announcement of less than 100kg/annum is introduced. 35 items of information, including the acute oral toxicity, are required to be notified to the Member State where manufactured or where the importer is established; the delay time, after receipt and before marketing, is proposed at 15 days.

Table 11

Comparison of 6th Amendment and proposed 7th Amendment

LIMITED ANNOUNCEMENTS" CONTINUED I.E.REDUCED LEVEL NOTIFICATIONS

PROPOSED 7TH AMENDMENT LESS THAN 100KG/YEAR
Identity, Information on the Substance (35 items); Physical state, Flash point, Flammability and acute toxicity — To THE Member State where manufactured, or where importing Notifier is established.
MARKETING DELAY — 15 DAYS

IN ALL CASES, LABEL —

CAUTION — SUBSTANCE NOT YET FULLY TESTED

Table 12 — Three low quantity exemptions cover (a) less than 1 tonne/annum "intended solely for laboratories" (ie laboratory chemicals?), (b) less than 100 kg/annum "for scientific R&D under controlled conditions in the laboratory" and (c) less than 10 kg/annum. No conditions are proposed for (a) and (c), but for (b) written records of identity, quantities and customers must be kept and made available to each Member State authority "upon request". To be eligible, these substances must not be "very toxic" or "toxic" under EEC rules.

Finally, a new symbol is proposed to cover the classification "dangerous for the environment". Criteria for classifying substances under this symbol have not yet been officially published, but are expected soon.

As you can imagine, these proposals have been subject to considerable discussion between authorities and chemical groups before reaching this stage. They must still be subject to further debate by the Economic and Social Committee and the European Parliament, after publication in the Official Journal. These proposals are, therefore, unlikely to be in force before 1992.

Table 12

Comparison of 6th Amendment and proposed 7th Amendment

"EXEMPTIONS"
6TH AMENDMENT
LESS THAN 1 TONNE/YEAR INTENDED SOLELY FOR LABORATORIES
No conditions
PROPOSED 7th AMENDMENT
LESS THAN 100KG/YEAR "SCIENTIFIC R&D UNDER CONTROLLED CONDITIONS IN THE LABORATORY"
Must maintain written records of Substance identity, Label, Quantities and Customer list — To be made available to EACH C.A. where mark "UPON REQUEST"

LESS THAN 10KG/YEAR
No conditions (provided not "VERY TOXIC" or TOXIC")

IN ALL CASES, LABEL —
CAUTION — SUBSTANCE NOT YET FULLY TESTED ∎

Carew et al, continued from p401

13. Bellenger, V. and Verdu, J. *J. Appl. Polym. Sc.* 1983, **28**, 2677.
14. Schweinsberg, D. P. and George, G. A., "A Chemiluminescence Study of the Properties and Degradation of Epoxy Resins as Coatings". Corrosion Science, 1986, **26**(5), 331.
15. Jeandrau, J. P., "Investigation into the Effect of Surface Treatment on the Wettability and the Bondability of Low Surface Energy Materials", Adhesive Joints, Formation, Characteristics and Testing, Ex. Mittal, K. L., *Plenum Press*, New York, 1984, 121. ∎

the fire protection system has is through its mesh system which has to be thoroughly mechanically attached.

The second purpose for wire mesh reinforcement is to reduce the considerable difference in expansion and contraction between epoxy intumescent and substrate steel. With a thick film epoxy system, the expansion and contraction differences are considerable and place a very high shear stress on the interface between the epoxy intumescent, primer and substrate steel. Our own tests have shown that wire mesh reinforcement mechanically attached to the substrate significantly reduces shear stress. Tests have also shown that thick film epoxy materials applied without mesh and subjected to accelerated temperature cycling will eventually lose their bond to the substrate.

The future for epoxy intumescent products offshore

As a manufacturer we are seeing an encouraging increase in the use of epoxy intumescent fire protection for offshore structures. The benefits of these materials are becoming to be recognised by operators who can see the advantages both in the construction and operation of platforms. The market itself, however, has limited growth potential because of the phasing of offshore developments.

Textron Speciality Materials have recently launched an improved version of Chartek 59 known as Chartek III. This material has significant improvements in terms of thermal performance. This is shown by the much reduced coating thickness in comparison with competitive epoxy intumescent products for hydrocarbon fire protection of structural steelwork.

The way forward for epoxy intumescents will be for further improvements in their thermal efficiency and, therefore, weight when applied to a structure whilst still maintaining the significant benefits afforded by them as they are now presented. Textron Speciality Materials intend to continue to be at the forefront of epoxy intumescent technology. ∎

The preparation of films from aqueous solutions of polyelectrolytes

by E. A. Wasson, H. M. Anstice* and J. W. Nicholson, Materials Technology Group, Laboratory of the Government Chemist, Queen's Road, Teddington, Middlesex TW11 0LY, UK
*Newnham College, Cambridge, CB3 0DF, UK

Abstract

The ability of waterborne coatings to form adequate films on practical substrates is important for the satisfactory deployment of such coatings. In the present study, designed to model film spreading by aqueous polyelectrolyte solutions, polymers and copolymers of acrylic acid were used to prepare films on various metal substrates. Solutions of poly(acrylic acid) at various degrees of neutralisation were studied extensively, and the concept of critical degree of neutralisation, α_c, developed. This value represents the highest degree of neutralisation at which acceptable films could be formed. The value of α_c was found to depend on polymer molar mass, nature of the neutralising species, and to a slight extent, film thickness and temperature. The use of surfactant to aid film spreading presented problems, since at certain degrees of neutralisation the whole system became cloudy; such cloudy systems were found not to form films. Finally, it was found that increasing the degree of neutralisation in a butyl acrylate/acrylic acid copolymer also led to poor film formation, so that the concept of a critical degree of neutralisation appeared to apply to these systems too.

Introduction

Since the introduction in Los Angeles of the now-famous "Rule 66" in 1966, aimed at reducing the emissions of organic solvents, a great deal of interest has been shown in the development of waterborne coatings[1,2]. These coatings are advantageous because water is ecologically acceptable and readily available in the industrialised regions of the world.

Typically polymers for use in waterborne coatings are made soluble or dispersible in water through the presence of polar groups within the macromolecule[2]. These polar groups are usually carboxylic acids or amines, and solubility or dispersibility of the polymer is improved by their neutralisation. Whether neutralised or not, the presence of ionogenic functional groups in the polymers used for these coatings means that they can be considered to be dilute polyelectrolytes[3]. There is no authoritative definition of the term "polyelectrolyte", but they are usually considered to be those polymers carrying a high density of ionic functional groups[4]. The fact, though, that waterborne resins will migrate between electrodes under the influence of a potential difference in aqueous solution, and hence can be used in the technical process of electrocoating, means that they must be considered to be some sort of polyelectrolyte.

Despite the importance of the process of film spreading to the successful application of waterborne coatings, the factors influencing the spreading of polyelectrolyte solutions have received very little attention. However, Myers and his co-workers have studied film spreading in such a system, using aqueous solutions of poly(acrylic acid) at different degrees of neutralisation[5,6], with fused quartz as the substrate. They considered poly(acrylic acid) to be an acceptable model for polyelectrolyte-based coatings[6], and studied the kinetics of drying of 100 μm thick films and the variation in water

retention with degree of neutralisation. They found that with increasing degree of neutralisation, α, there was an increased amount of water retained in the film, as well as a corresponding reduction in the rate of drying[5,6]. In addition, as the film changed from the liquid to the solid state, so the rate of drying was found to slow down. Then, once in the solid state, the rate of drying appeared to be influenced by the size of the metal counterion, large ionic radius being associated with slower rate of drying[5]. This effect was found to be even more pronounced when organic amines were used, and films containing them as neutralising agents remained tacky for up to 4 hours after spreading, whereas films containing metal ions were touch dry after only one hour.

These findings by Myers et al contrast in an important respect with more recent work of Nicholson et al[7-9] on the preparation of coatings from partially neutralised poly(acrylic acid). These latter papers emphasise the novel cure chemistry that can be facilitated by the presence of a small proportion of sodium carboxylate groups (5-10% of total carboxylate) within the polymer. This chemistry consists of anhydride formation by the free acid groups at elevated temperatures, followed by decarboxylation to yield keto crosslinks, and the various publications describe the process and give data on the properties of the resulting coatings. In passing, however, Nicholson et al have noted that film spreading is impeded by excessive neutralisation, and that at levels of sodium carboxylate of 25% or above, films as such do not form. Instead, on removal from the stoving oven, substrates were found to be mainly free of any coating, and to have on them a few isolated globules of polymer which had clearly reticulated severely[8].

The conditions for film spreading used by Nicholson et al varied in three ways from those used by Myers et al. Firstly, films were extremely thin (approx 5 μm, compared with 100 μm); secondly, realistic substrates were used, i.e. aluminium and tinplate rather than fused quartz. Finally, a trace of commercially available non-ionic surfactant was added to each formulation to aid film spreading. By contrast, in the latter studies, no surfactant had been necessary, since films could be spread readily on the fused quartz substrate employed.

The present study was undertaken in order to examine which of these differences were significant in influencing film spreading, and to resolve the apparent disagreement between the two sets of work. The study has consisted of an extensive examination of film formation by aqueous solutions of partially neutralised poly(acrylic acid) and more limited studies of systems that incorporate surfactant, and/or contain an acrylic acid copolymer as the principal film former. The work with partially neutralised poly(acrylic acid) solutions was designed to establish the influence of molar mass, film thickness, temperature and nature of the counterion on film spreading, whilst the studies with systems containing surfactant and/or copolymers were aimed at extending initial findings to coatings systems of greater practical importance.

Materials and methods

Poly(acrylic acid) [ex Allied Colloids, Bradford, Yorkshire] samples of differing molar mass were partially neutralised with LiOH, NaOH, KOH, morpholine or ethanolamine. The neutralising agents were generally of Analytical Reagent Grade. Solutions were prepared at varying degrees of neutralisation and at solids concentrations equivalent to 15% PAA.

The prepared solutions were coated onto "Alodyne"—treated aluminium panels [ex Q-Panel Co., Salford, Greater Manchester] using a wire-wound K-hand coater [ex RK Print-Coat Instruments Ltd., Royston, Herts]. This substrate was used because, at certain degrees of neutralisation, films remained spread on it without any surfactant being incorportated into the wet formulation.

For studies of the effect of surfactant, one drop of Triton X-114, a non-ionic surfactant [ex. BDH, Poole] was incorporated into the solution and films were spread on untreated aluminium.

For studies with copolymers, an acrylic acid/butyl acrylate copolymer (11% acrylic acid : 89% butyl acrylate diluted to 15% solids) was used. This was in the form of a latex, but became soluble on neutralisation with sodium hydroxide solution. Formation of films from this polymer was attempted on tinplate and untreated aluminium using the 6 μm K-Bar.

The coated panels were dried in air for at least one hour before being assessed visually for coating quality. Films appeared either apparently perfect, or clearly defective. In the latter case, imperfections showed up as craters of uncovered substrate or as receding away from the edge of the panels ("crawling").

In order to determine what factors affected substrate wetting by partially neutralised poly(acrylic acid), the following parameters were varied.

1. Degree of neutralisation (α): this was varied between 0-100% in 5% increments. The critical degree of neutralistion (α_c) was defined as the highest degree of neutralisation at which a perfect coating could be obtained. All other parameters were assessed in terms of the effect they had on α_c.

2. Neutralising agent: The neutralising agents used were LiOH, NaOH, KOH, morpholine and ethanolamine.

3. Molar mass of poly(acrylic acid): Four different samples of poly(acrylic acid) were used, having different molar masses and polydispersities, as shown in Table 1.

Table 1

Molar masses of poly(acrylic acid) used.[12]

Poly(acrylic acid) sample[*]	M_n	M_w	M_w/M_n
E5	7300	11500	1.58
E7	11300	22700	2.01
E9	40400	114000	2.82
E11	112000	383000	3.42

([*] ex Allied Colloids, Bradford).

4. Film thickness: In these studies a standard wet film thickness of 6 μm was used, as determined by the choice of K-Bar used for film spreading. To determine the effect of thickness on spreading, films were also prepared at 24 μm and 50 μm.

5. Temperature: The above studies were all conducted at room temperature, which varied from 20.0°C to 24.5°C. In order to determine the effect of temperature on film formation the plate, solution and pipette were heated to 30°C, 40°C or 50°C before spreading the coating. In addition, a further set was cooled at 6°C. Two solutions were examined, namely 60% and 70% neutralised sodium

polyacrylate (sample "E7"; see Table 1). Coatings were applied at 6 μm film thickness.

Results and discussion

The results of this investigation are detailed in Tables 2 to 4. Table 2 illustrates the method by which α_c was determined from a typical series of film spreading experiments.

Table 2

The determination of α_c values for sodium neutralised poly(acrylic acid) on Alodyne-treated aluminium.

$\alpha(\%)$	Poly(acrylic acid) grade			
	E5	E7	E9	E11
5	1			
10	1			
15	1			
20	1			
25	0	1	1	1
30	0			
35	0			
40				
45				
50	0	1	1	1
55		1		
60		1		
65		0	1	1
70		0	1	1
75	0	0	0	0
80			0	0
85				
90				
95				
100	0	0	0	0
$\alpha_c(\%)$	20	60	70	70

(0 = poor film; 1 = good film)

Table 3

Effect of molar mass and neutralising agent on α_c values for E7 poly(acrylic acid) on alodyne-treated aluminium.

Neutralising Agent	$\alpha_c(\%)$			
	E5	E7	E9	E11
LiOH	50	80	100	100
NaOH	20	60	70	70
KOH	35	60	90	90
Morpholine	25	45	60	70
Ethanolamine	15	55	80	85

Wet film thickness = 6μm. Temperature = 22°C.

Table 4

Effect of film thickness on α_c for E7 poly(acrylic acid) on Alodyne-treated aluminium.

Neutralising agent	α_c at film thickness		
	6 μm	24 μm	50 μm
LiOH	80	75	75
NaOH	60	55	55
KOH	60	55	55
Morpholine	45	40	40
Ethanolamine	55	50	50

PAA = E7, Temperature = 22°C

The effect of neutralising agent on α_c is illustrated in Table 3. This shows that the higher values were obtained for those films containing the metal ions, though there was no clear

trend in the values going down Group I of the Periodic Table from lithium to potassium. Large ions would be expected to restrict polymer chain motions to the greatest extent, and this in turn would be expected to increase solution viscosity and thus inhibit the development of imperfections in spread films. Hence it might have been expected that α_c would increase down the Group. This means that lithium seems to be exhibiting anomalous behaviour, probably due to the site binding of the metal ions. This site binding behaviour is known to be exhibited only by lithium amongst the Group I metals[10,11], and would be expected to alter the net charge on the macromolecule, and in turn lead to the anomalous value of α_c observed.

Within the limits of molar mass studied, α_c was found to rise sharply before reaching a plateau at high molar mass (see Figure 1). The fact that high molar mass solutions remained spread was probably due to the greater viscosity. As mentioned previously, development of imperfections would be expected to be favoured in those films that remain relatively mobile, and so therefore these findings are consistant with such an expansion.

Film thickness appeared to have only a marginal effect on α_c which decreases slightly with increasing film thickness (see Table 4). This was probably due to the fact that thicker films take longer to dry out, and so retain their mobility for longer than thinner ones. This allows imperfections to develop as the wet film flows away from certain areas of the substrate. Hence the fact that Myers and his co-workers[5,6] used thick films was not the reason that they were able to form films at all values of α up to 100%. Instead their use of a very different substrate, fused quartz, was almost certainly the reason for their success with this aqueous system.

As with film thickness the effect of temperature appeared to be minimal. At temperatures above ambient there was no detectable change in film spreading ability. Below ambient however the film quality deteriorated and α_c dropped to 45%

for the system examined, i.e. sodium neutralised E7 poly(acrylic acid).

The effect of surfactant was examined by adding one drop of Triton X-114 to 10 ml samples of aqueous formulations of partially neutralised poly(acrylic acid). Films were then spread at 6μm using these formulations onto untreated aluminium panels. Critical degree of neutralisation values were established for each counterion employed, as shown in table 5, and these were compared with the cloud point for each solution.

Table 5

α_c and cloud point values for partially neutralised E7 poly(acrylic acid) on untreated aluminium using Triton X-114 as surfactant.

Neutralising agent	$\alpha_c(\%)$	Cloud point (%)
LiOH	45	>50
NaOH	30	30
KOH	25	30
Morpholine	15	20
Ethanolamine	25	30

For adequate film spreading on this substrate, it can be seen that α_c correlates with the cloud point, regardless of which counterion is used. In this case, it seems that the main influence on film spreading is the effectiveness of surfactant, which clearly deteriorates as the surfactant ceases to be miscible with the aqueous phase. This development of cloudiness is a well-known phenomenon with surfactants, and is an example of "salting-out" by adding an electrolyte to alter the solvating action of water[4].

Finally, films were prepared on tinplate and aluminium using aqueous solutions of partially neutralised acrylic acid/butyl acrylate copolymer, with non-ionic surfactant

Figure 1

Critical degree of neutralisation (α_c) v. molecular weight (M_n) for partially neutralised poly(acrylic acid) in water on Alodyne-treated aluminium. [Neutralised by: K^+, Na^+, Li^+, morpholine and ethanolamine].
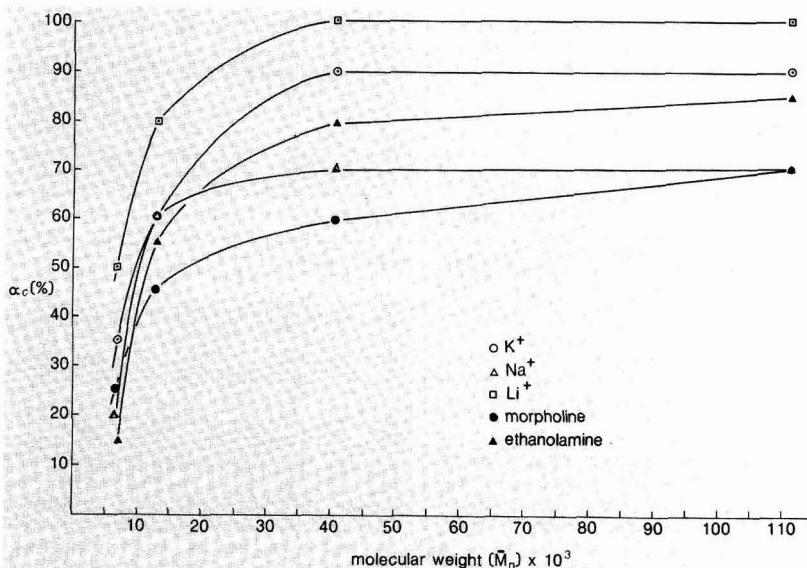
present. Once again, as shown by the results in Table 6, there was a limit of neutralisation above which satisfactory films could not be spread. Since these systems were already cloudy, it was not possible to determine whether or not the values of α_c found corresponded to the limit of surfactant effectiveness, as previously. However, the fact that an essentially similar phenomenon was observed for this latter system indicates that the problem of substrate wetting at higher degrees of neutralisation is a general one for aqueous coatings based on polyelectrolytes.

Table 6

α_c values for partially neutralised acrylic acid/butyl acrylate copolymer with non-ionic surfactant on different substrates.

Counterion	α_c (% on copolymer mass)	α_c (% of acid groups)	Substrate
Na^+	5	82.4	Tinplate
Na^+	5	82.4	Untreated aluminium

Conclusions

This study has confirmed the observation that where metal, as opposed to fused quartz, substrates are used partially neutralised poly(acrylic acid) can be spread as films only up to a certain point, defined as the critical degree of neutralisation. In addition to the nature of the substrate, the critical degree of neutralisation has been found to depend upon (i) the choice of counterion, (ii) the molar mass of the polymer, and to slight extents, (iii) the thickness of the wet film and (iv) the temperature at which films are spread. Where surfactant was present, its effectiveness was also found to depend upon the extent of neutralisation, with higher values leading to phase separation, and causing the surfactant to cease to function as a wetting agent. Finally, experiments with the copolymer electrolyte acrylic acid/butyl acrylate showed that it, too, exhibited problems of unsatisfactory film spreading at higher degrees of neutralisation.

References

1. Martens, C. R., "Water-borne Coatings", 1981, *van Reinhold*, New York.
2. Nicholson, J. W., "Waterborne Coatings", OCCA Monograph No 2, 1985, *OCCA*, London.
3. Beck, F., in Wilson, A. D. and Prosser, H. J. (Eds), "Developments in Ionic Polymers". Vol 2, 1986, *Elsevier Applied Science Publishers*.
4. Vold, R. D. and Vold, M. J., "Colloid and Interface Chemistry", 1983 *Addison Wesley*, Massachussets.
5. Tsutsui, K. and Myers, R. R., *Ind. eng, chem, Prod, Dev*, 1980, **19**, 310.
6. Raju, K. S. and Myers, R. R., *J. Coatings Technol.*, 1981, **53** (676), 31.
7. Nicholson, J. W. and Wilson, A. D., *Chem. & Ind.*, D., J. 530.
8. Nicholson, J. W., Scott, R. P. and Wilson, A. D., *JOCCA*, 1987, **70**, 157.
9. Nicholson, J. W. and Wilson, A. D., *JOCCA*, 1987, **70**, 189.
10. Klooster, N. T. M., van der Trouw F. and Mandel, M., *Macromolecules*, 1984, **17**, 2087.
11. Klooster, N. T. M., van der Trouw, F. and Mandel, M., *Macromolecules*, 1984, **17**, 2070.
12. Hill, R. G., Warrens, C. P., Lewis, B. G. and Wilson. A. D., *J. Mater. Sci.* 1989, **24**, 363. ∎

OCCA Meetings

Transvaal Section: ERNII

On 21 June the Section was addressed by Ms Cherylynn Wilson and Mr Mike Boulanger of the firm ERNII (Electronic Reference Network for Industrial Information).

ERNII is a computerised database designed to assist users to obtain information and to update their product and service data. Access to ERNII is via Beltel. The system saves time and allows direct communications between users and suppliers. Security features are incorporated to protect the confidentiality of all information.

The system offers search facilities for information on companies products, services and brand names. Enquiries, quotations, orders and messages can be sent and received at any time.

ERNII offers a tender bulletin for the major state and parastatal institutions. Tender details are instantly available to the supplier and may be selected by product category.

After a presentation by Mr Boulanger of the facilities offered by ERNII a practical demonstration of the ease and versatility of the system was given by Ms Wilson.

After an active question and answer session the vote of thanks proposed by Mr Peter Quorn was heartily endorsed by the 21 members and 4 guests.

R. E. Cromarty ∎

Classified Advertisements

INSTRUMENTATION

ACM Instruments

ELECTROCHEMICAL INTERROGATOR SERIES

Faster Environmental testing is now possible with an improved degree of accuracy and reproducibility by recent developments in electrochemical instrumentation. Up to 32 environmentally exposed painted samples can now be tested by potentiodynamic AC or DC techniques simultaneously around their individual rest potentials in the same test environment and test tank. This increases testing reproducibility as all samples are treated in exactly the same way with no difference in temperature or emersion time of the electrodes before and during testing. For information and demonstration software:
Telephone or Fax (0706) 64377
Faraday House, 2 Middleton Road, Heywood, Lancs OL10 2BT.

Enter J304 on Reader Reply Card

Classified Advertisements