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April 1988

JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION

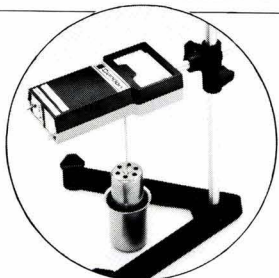
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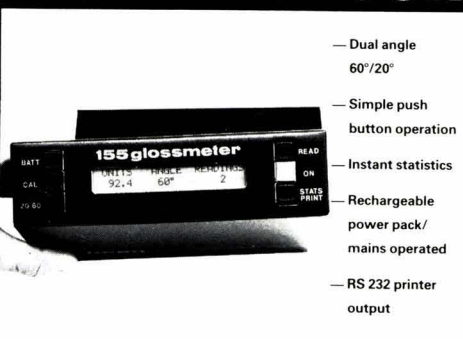
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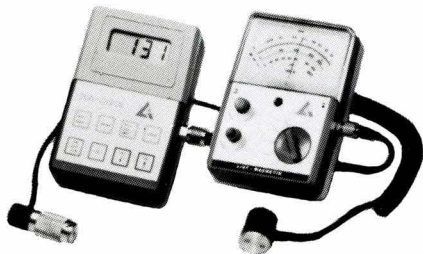
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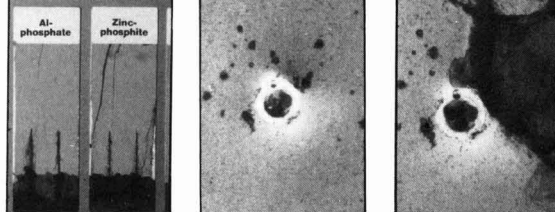
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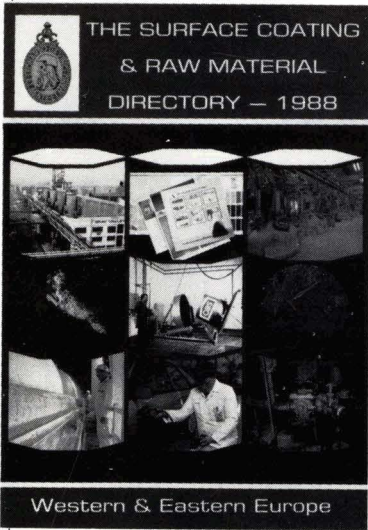
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From the President

Congratulations to JOCCA on reaching its 70th Anniversary. It is regarded as a high class scientific publication and is one of the foremost in its field in the world. Its objectives are to publish scientific and technological papers of high standards of ability and originality, covering aspects of the industries it services and to report the technical and social activities of the Oil & Colour Chemists' Association and its Sections.

Your Publications Committee have recently been considering how JOCCA can maintain its enviable scientific quality reputation and also its financial viability.

After thorough consideration of various proposals, to which we are indebted to our General Secretary, they unanimously agreed to some changes in appearance to provide JOCCA with a modern image, more attractive to advertisers whilst still maintaining the quality of its technical content. We sincerely hope you will approve the redesigned front cover and note that the internal layout has been changed to enable the Assistant Editor and printers to produce the Journal more efficiently and on time. If successful, these changes will also encourage increased circulation and advertising revenue, JOCCA will then be sure of reaching its 100th Anniversary.

Please write and let us know if you approve the new style, and don't hesitate to tell us any further ideas which might further enhance JOCCA. The international reputation of the Journal has been built on the quality of research and technical articles printed in JOCCA, your ideas on how to maintain an adequate supply of such articles would be particularly welcome.

J. R. Bourne ■

Editorial

Protective Coatings – Has the Surface Coating Industry risen to the present challenge?

The value of protective coatings is becoming more and more important to industry and to the general public due to the high cost of replacement and repair.

It was not so long ago before the introduction of thermally cross-linked acrylic and epoxy resins into formulations that finishes for refrigerators and washing machines could become softened and stained or even removed by such every day simple materials as boot polish, lipstick, butter or washing powders. The present day specifications for coatings for the domestic appliance manufacturers are such that high performance finishes are essential to pass the requirements.

In the automotive industry corrosion resistance and retention of colour and gloss of finishes applied have become an important part of the sales strategy of the industry and a guarantee of corrosion resistance given by a particular car manufacturer is of great importance to the purchaser of the car. Again the use of new and more advanced organic and inorganic coatings and modification of construction has allowed coatings to be applied in areas where corrosion is to be expected. The increase in the amount of salt and grit applied to the roads during winter has been a contributing factor for the requirement of better protective coatings.

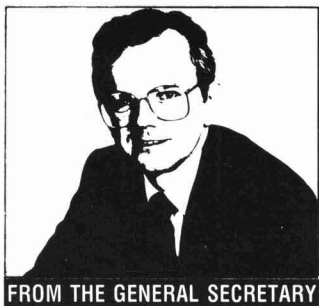
In the chemical, oil and marine industries the need for protection is paramount and particularly in the North Sea where oil and gas platforms must be maintained free from corrosion at all times when the application of coatings must often be applied under less than perfect conditions and yet are expected to give the required performance. The same long-term protection is needed for the road bridges on motorways.

The Surface Coating Industry has formulated these coatings by the use of often new or modified resins and in the case of anticorrosive coatings, new pigments. The attention to toxicity and the effect on the environment has become an additional and important new limitation placed on the formulator. The fact that red lead and chromate based pigments, which in the past have given reasonable resistance to corrosion, have become restricted in use, due to their toxicity has required a radical change in attitude regarding anti-corrosion formulation.

The importance of this new challenge has been met by research and development and is clearly indicated by the introduction of new families of less toxic anticorrosive pigments with useful work being undertaken to elucidate the mechanism of corrosion. This is demonstrated by the excellent standard of papers which have been written to explain the inhibitive properties of the various pigments such as zinc phosphate, molybdates, silicates, the new base exchange types (Shieldex) and the metal glasses.

The rheological properties of protective coatings have had to be investigated in order to be able to apply high build products to vertical surfaces, again this is an important property in reducing the time and cost involved in coating structures.

The answer to the original question posed in the Editorial is that the Surface Coating Industry has therefore applied the necessary technical knowledge to meet the present challenge but no doubt further work will be required in the future and it is hoped that workers in this important field will submit their papers for publication in the Journal of the Association, especially for the feature on anticorrosion coatings in September JOCCA. ■



FROM THE GENERAL SECRETARY

JOCCA

It is most appropriate that in its 70th year of publication, the Association's Journal and its principal publication should undergo a major relaunch. This first edition of the new style *JOCCA* is manifest not only by a new design and layout, including for the first time full colour on the front cover, but also introduces a major change in Editorial policy.

JOCCA has a long and internationally respected tradition for quality research and technical papers and this is a tradition that the Association's Council is committed to maintain. At the same time the Journal exists in a fiercely competitive world in which several other commercial and learned society publications are competing for subscribers and advertising income. The Association must respond to these challenges, given its more limited resources, to produce a Journal worthy of the Association, but also be commercially viable.

I believe that the new editorial policy will ensure the success of both these, perhaps conflicting, objectives:

An editorial programme will ensure that each issue features a topic of interest to members, subscribers and the industry. Our editorial programme will be published for some months in advance, but will be sufficiently flexible to ensure that events of importance can still be slotted into the programme at short notice.

Protective coatings are featured in this issue and the following topics will appear in the remaining issues during 1988:

May SURFEX 88 – Official Guide
June Support Services for the Paint Industry
July Resins
August SURFEX 88 – Report
September Anti-Corrosion Coatings
October Additives in Paint
November Total Quality Assurance
December Painting of Concrete

In addition to these special topics, the Journal will also feature news of companies, the products and personnel – together with expanded news of the Association and its activities. Other initiatives are planned, involving collaborative features with other relevant organisations.

You will notice that this issue also includes a comprehensive Reader Reply and OCCA Membership Enquiry Service. Please make use of these facilities to seek further information on the products featured in the Journal, to request membership information or to notify Priory House of membership changes.

SURFEX

Regular readers of *JOCCA* will have hardly failed to notice that SURFEX 88 will be taking place in Harrogate on 15-16 June. The first SURFEX Exhibition in 1986 was a new venture for the Association and was a major success. SURFEX 88 is larger and fully booked and is established as the leading UK exhibition of the Surface Coatings Industry. The March *JOCCA* carried an eight-page update to the Exhibition and the Official Guide will feature in the May issue. UK and European based readers will find complimentary SURFEX invitations with this issue of *JOCCA* – overseas readers will have received their tickets in the March issue. Please make use of these tickets, either by visiting the

Exhibition or passing the tickets on to colleagues who are able to attend. Additional tickets are available from OCCA headquarters.

AGM

Associated with the Exhibition will be the Association's Annual General Meeting on Wednesday 15 June. AGMs are traditionally regarded as dull, rather legalistic meetings, but any member visiting SURFEX should include the AGM in their diary. After all, it is the most important meeting in the Association's calendar and gives any member the right to question the Association's officers on their stewardship of the Association's affairs.

We look forward to seeing you in Harrogate. You will find the OCCA stand in the Reception area by the registration desk. Pay us a visit – all members, readers and visitors will be given a warm welcome.

Chester 89

Despite the activity surrounding SURFEX the Association's Biennial Conference occupies much staff and officer time. The Chester Conference promises to be as innovative and exciting as SURFEX and the Journal relaunch. Honorary Officers Tony Jolly and John Taylor are putting together an excellent technical and social programme.

The topic "Profitable Research & Development" is a new theme for an OCCA Conference and is worthy of support. A call for papers has already gone out and some offers of papers have been received. However, we are still looking for additional good quality papers for presentation at Chester and subsequent publication in *JOCCA*. If you feel you have something to say on this topic please contact me or write to John Taylor at Priory House. ■

ICI and DuPont car paints European link up

ICI and DuPont are merging their European motor vehicle operations. The headquarters of the joint venture will be located in Bonn, W. Germany. The two companies will provide £25m which will include the development of a £10m R & D Centre at Bonn followed by a manufacturing plant. Brian Letchford, one of ICI Paints directors, stated that the aim was to become the market leader in this sector over the next few years. The joint company will start with a 10% share of the European motor vehicle paints market worth £500m a year with the object of quickly building up to 20%. The new company will start in fourth place in the European market which is headed by BASF. The worldwide market is estimated at 600m litres of paint worth £1.3 billion. The new company will consist of an existing R & D staff of 500-strong working on motor industry paint coatings.

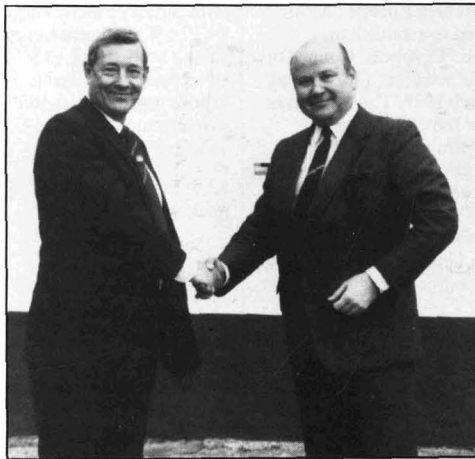
ICI profits rise to £1.31bn

ICI's pre-tax profits increased by 29% (£306m) to £1.31 billion in 1987 helped by strong performances in the paints, chemical and polyurethane divisions. The consumer and speciality products subsidiaries increased trading profits from £507m to £574m helped by the acquisition of the American Paint Company, Glidden.

Williams profits up

Williams Holdings has announced a 169% profits rise to £57.2m on a turnover of £463m last year following the acquisitions of Berger and Crown which made the former Welsh foundry second only to ICI in the UK paint market. In the days following their profits announcement they have sold Elastomers for £7.5m to the Products Research & Chemical

Granyte forms new European company



Granyte Surface Coatings Chairman William Jinnat (left) and Jean Michel Wyns of Wyns-Bristol, seal the foundation of Belgium-based NV Granyte.

Granyte Surface Coatings plc has formed a new European sales and marketing operation, in association with Belgian paint manufacturer Wyns-Bristol. The jointly-owned company, NV Granyte, will be based in Vilvoorde, north of Brussels. Current Granyte Surface Coatings Chairman William Junner will also

chair the associate company, whilst his opposite number at Wyns-Bristol, Jean Michel Wyns, joins him on the board and will serve as acting General Manager. Complementary manufacturing capabilities mean there is little overlap with Wyns-Bristol's decorative products and Granyte's range of quality wood finishes and high performance industrial paints. NV Granyte will concentrate on the Benelux and Italy areas.

Corporation of California and then bought from the Standard Brands Paint Company, Kwal-Howells for £4.38m. Williams profits this year are expected to be in the range of £115m allowing scope for further acquisitions.

Wacker-Chemie increases influence in Italy

Wacker-Chemie has increased its shareholding from 50% to 97% in its Italian sales and marketing subsidiary which has been purchased from its partner, B. H. Schilling SpA. The company's name will be changed to Wacker-Chemie Italia SpA. The firm will be head quartered in Milan with Friedhelm Graf remaining as Managing Director.

Ellis & Everard acquire Colt

Ellis & Everard plc, the UK's leading independent chemical distributor, has acquired the Colt Chemical Co of Leeds. Colt operates as chemical processors involving commission drying, mixing and blending of chemicals. The acquisition by Ellis & Everard enhances the Group's interests in the chemical services sector.

Creation of the European Council of Vinyl Manufacturers

Presently 12 million tonnes per year of PVC are produced worldwide to meet market demands. The PVC producers

within the Association of Plastics Manufacturers in Europe (APME) have decided to establish in Brussels the "European Council of Vinyl Manufacturers" (ECVM) as from 1 March 1988. The objectives and tasks of the ECVM are to promote better understanding of PVC products, to provide access to worldwide data about PVC, to initiate studies and research on health and environment related issues, to communicate existing and potential solutions related to the safe handling and use of PVC. ECVM will be staffed by a small permanent team headed by Dr W. Freiesleben as Director. The Council's address is ECVM, 250 Avenue Louise, Box 122, B - 1050 Brussels, Belgium.

ICI Paints Japanese agreement

ICI Paints has entered an agreement for exchange of technology with Nippon Oil and Fats (N.O.F.), a major Japanese chemicals concern and a leading supplier of paints to the Japanese automotive industry. Under the terms of the agreement, ICI Paints technology developed for the automotive industry will be available, under licence, to N.O.F. in Japan and other parts of the world whilst N.O.F. technology becomes available, on the same basis, to ICI Paints in Europe, North America and other parts of the world. It also relates to production by ICI of N.O.F. approved paint formulations for sale to Japanese car companies manufacturing in these territories and production by N.O.F. of ICI Paints formulations for sale to car plants in Japan and other parts of the world. The agreement was signed in Japan by the Principal Executive Officer of ICI Paints, Herman Scopes, and the President and Chief Executive Officer of N.O.F., Kineo Okamoto.

Johnstone's Paint Buoyant

Record sales were again

achieved by Johnstone's Paints plc with turnover increasing to £16m (+10.5%) with pre-tax profits falling to £1.81m (-12%) as a result of increased raw material and labour costs exacerbated by price discounting within the UK paint industry.

Reed invests £3.6 million in plastic packaging plant

Reed Plastic Containers has announced that it is to expand its capacity by setting up a new manufacturing plant in the North West of England. Representing an initial investment of some £3.6 million, the operation will be located in a recently acquired 105,000 sq ft factory in Blackburn, Lancashire. This is situated on a 23 acre site which provides space for further expansion. Reed's move reflects the accelerating changover to plastic containers for marketing many types of products previously distributed in glass and tinplate packaging. It also underlines the company's continuing commitment to the paint packaging markets. The Blackburn plant is scheduled to begin production in April 1988. The new site will provide much-needed additional space for manufacture of a variety of injection-moulded containers, including a number of new plastic packaging developments to be introduced by Reed in due course.

Macphersons expands colour range for protective coatings

It is no longer acceptable to provide protective coatings in drab colours with the emphasis purely on protection. The explosion of colour awareness and the requirement for pleasing aesthetics is now as much a pre-requisite for heavy duty anti-corrosion systems as it has been in the trade decorative market. It is for this reason that Macphersons has opened a £1m heavy duty production plant at its Bury headquarters, Lancashire. This unit has been designed to give one of the most flexible modern

manufacturing systems within Europe and it is planned to meet the requirements of industry well into the next century. The colour range will be available for the special finishes marketed under the brand name "Tema" used in the protection of steel and concrete structures, i.e. high build alkyd zinc phosphate primers, two pack and single pack pre-construction primers, high build zinc rich epoxy coatings, ethyl zinc silicate coatings, low build chlorinated rubber, bituminous and tar based coatings, alkyd intermediate finish coats, tank linings and polyurethane coatings. Over 1,000 product colours will be available including the complete BS4800 colour range. The new computer controlled plant production will allow preparation of one-off colours in large batches to as low as 5 litres within days of specification.

ENTER D100

New anti-delamination floor coating primer

London Chemical Co, manufacturer of synthetic resin-based building products, has available the Flexithane Super primer for reducing the all-too-common delamination failures, resulting from demanding impact and abrasion service conditions superimposed on a previously poorly prepared substrate (usual concrete), which itself is given to movement. The London Chemical Co recognised that frequently synthetic resin-based floor coating systems delaminated readily from their substrates (usually concrete) when subjected to aggressive service conditions. The causes were usually lack of primer, due to absorption into excessively porous concrete or lack of primer adhesive strength (often as a result of poor substrate preparation) or lack of primer resilience (that is the optimum combination of hardness and flexibility). Thus, after having looked at a wide range of primers representing varying polymer species, it was decided to dispense with conventional primers and to

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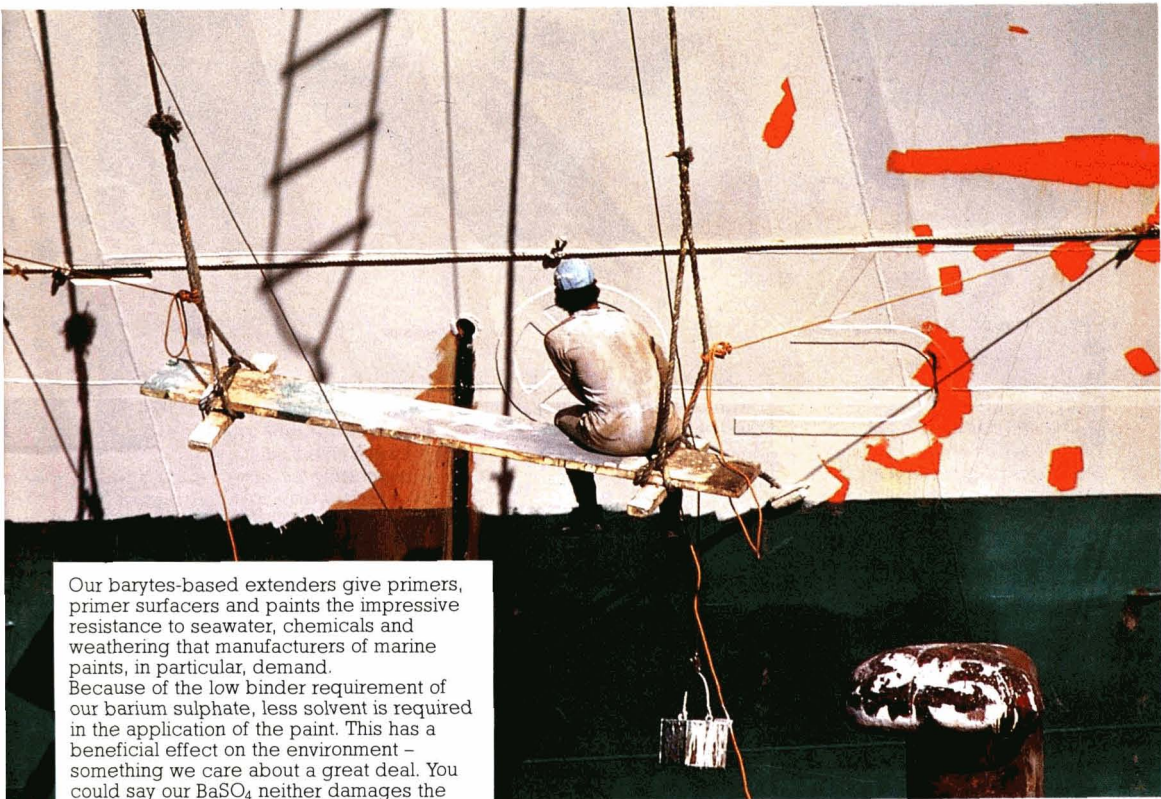
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pH value	DIN 53 200	approx.	8
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Particle size distribution %			
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			< 3 μ m
			< 2 μ m
			35
Brightness	DIN 53 163	approx.	92
Oil absorption g/100g	DIN 53 194	approx.	11
Sieve residue %*	DIN 53 195		< 0.05

*Test sieve 45 μ m

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Two new ranges of Sheen Instruments



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Sheenscope

Sheen Instruments has introduced a new range of high quality instrumentation for the measurement of coating thickness on most metal substrates. SE1000 offers full statistical analysis at the touch of a button as well as rapid calibration, automatic zero, rough surface measurement capability and a wide variety of probes to handle difficult areas such as curved surfaces, small components and the interior of pipes and tubing. SE1000 is available in three model versions: individual ferrous or non ferrous models, plus a combined version to measure on ferrous and non ferrous

substrates. SE1000 can be supplied with or without additional software to provide hard copy plus histogram.

Sheen has also introduced a range of instruments for measuring and inspection of surface properties called the Sheenscope. This gives accurate surface inspection at an inexpensive cost, in any location and at any time. The new Sheenscope instrument consists of X 100 magnification microscope built from RMS standard components and focusable through a 25 mm range by means of a rack and pinion. Incident illumination of

the surface is by means of a 2.5V battery lamp positioned within the microscope tube controlled by a switch on the handle. Three small supporting feet rest on the sample or surface to keep the instrument steady. For operation the red button is pressed to illuminate the surface and the focus control on the eye-piece is then adjusted to bring the surface into view. The Sheenscope is supplied in a lightweight case, which also contains a spare bulb, two spare batteries, a pack of lens tissues and a handbook and operating instructions.

ENTER D102

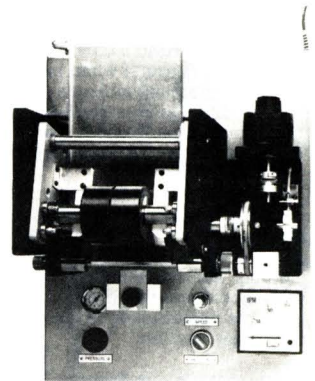
look at an equally wide range of adhesives. One was selected and found to be easily modifiable.

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New proof-press for litho and letterpress inks

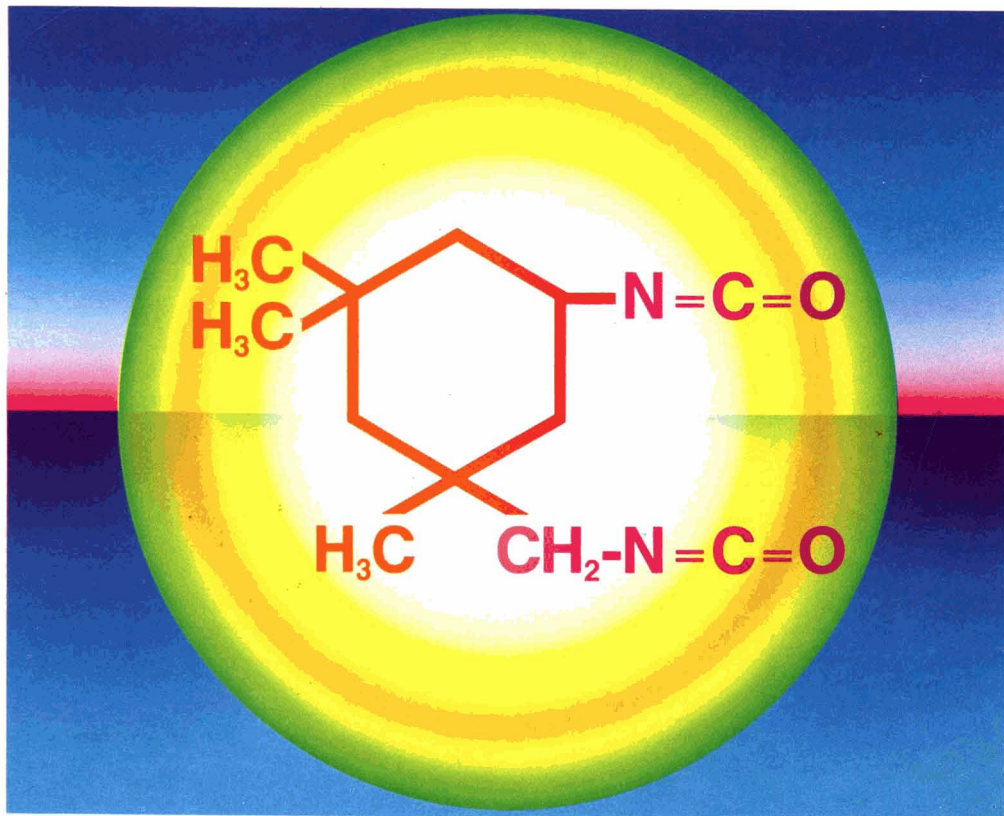
RK Print-Coat Instruments has developed a new Paste Ink Proofer which needs no operator training. The proof-press avoids the need to weigh or measure ink and the unified inking and printing sequence uses two rollers.

The PIP produces single colour proofs up to 82 mm wide and, by means of a split roller, two colour proofs each 35 mm in width. The third application of the PIP is in ink-density appraisal. A 'three-in-one' transfer roller comprising three bands of polyurethane (or similar plastic) is used to produce three 26 mm-wide side-by-side proofs for the quick appraisal of high, medium and low densities, when checking a new batch of ink. The 'three-in-one' roller is interchangeable with the rollers that produce either single-colour or two-colour proofs. The PIP proof-press can be used with the viscous inks employed in litho, webb-offset



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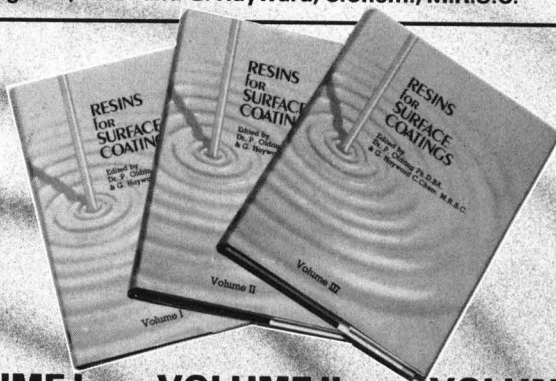
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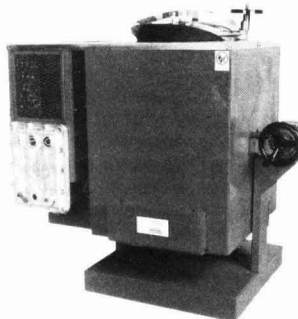
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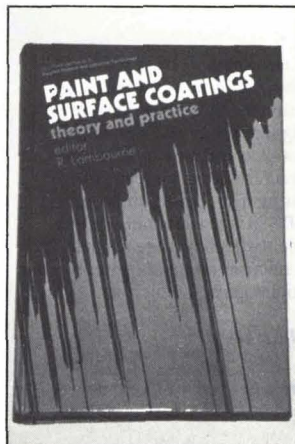
Paint and Surface Coatings

Theory and Practice



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

696 pages; Published April 1987; £79.50/\$152.75
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CONTENTS: Paint Composition and Applications—A General Introduction; Organic Film Formers; Pigments for Paints; Solvents, Thinners and Diluents; Additives for Paint; The Physical Chemistry of Dispersions; Particle Size and Size Measurement; The Industrial Paint Making Process; Coatings for Buildings; Automotive Paints; Automotive Refinish Paints; General Industrial Paints; An Introduction to Rheology; The Rheology of Paints; Mechanical Properties of Paints and Coatings; Appearance Qualities of Paint—Basic Concepts; Specification and Control of Appearance; Durability Testing.

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Surfactant Technology

Industrial Colloid Advisory Group (INCOLLAG) will hold an awareness forum on Surfactant Technology at Bristol University on 30 June 1988. Topics will include: Properties and Applications of Nonionic, Cationic, Fluorocarbon and Silicone Surfactants; Wetting, Solubilisation (Microemulsion), Foam and Concentrated Surfactant Systems. For further details contact: Mrs J. Proctor, Physical Chemistry Department, University of Bristol, Cantock's Close, Bristol BS8 1TS.

CEI - Europe

The 1988 Annual International Courses in Surface Engineering and Coating Technology will be held from 26-30 September 1988 at the Davos Congress Centre Switzerland. Subjects dealt with include wear protective coatings, optical coatings, electroplating technology, adhesion, polymer coatings: alternatives to solvent

based coatings. For further information contact: Elsevier Seminars, Penny Moon, Mayfield House, 256 Banbury Road, Oxford OX2 7DH, UK.

Marine Corrosion and Fouling

The 7th International Congress on Marine Corrosion and Fouling will be held in Valencia, Spain, on 7-11 November 1988. The Congress will be in two sections. Section I: Corrosion and protection of submerged metallic and non-metallic works. Section II Biological and bacteriological corrosion. For further information contact: Congress Secretary, Cátedra de Construcción III, Departamento de Construcciones Arquitectónicas, Universidad Politécnica de Valencia, Camino de Vera, s/n, 46022 - Valencia, Spain.

Reed Plastics appointments

As part of the expansion programme of its "Paintainer" range, Reed Plastic Containers has announced the appointment of Andrew Bloor as Paintainer Production Manager. Recently Mr Bloor was presented with the 'Jones & Shipman' cup, awarded to the best Diploma student by the Institution of Industrial Managers.

BASF C & I new appointments

The Refinish Division of BASF Coatings + Inks based at West Drayton which manufactures the leading automotive refinishing brands of Glasurit, Valentine and R-M, has made a number of new appointments to its technical and marketing departments.

Tom Smith has joined BASF Coatings + Inks as Technical Services Manager. Tom will be responsible for all aspects of technical services including training, colour and customer services.



New appointments at the Refinishing Division BASF Coatings + Inks (left to right): Gary Rudland, Valentine Brand Marketing Executive, Andy Shave, Technical Manager, and Tom Smith, Technical Services Manager.

Andy Shave has been promoted to Technical Manager. Andy, who joined Valentine in 1976, will be responsible for the product laboratory and manufacturing technical control for the Refinish Division.

Gary Rudland, previously Sales Office Manager, has been made Marketing Executive for the Valentine brand. Gary joined Valentine in 1976 and has spent 11 years overseeing the day-to-day running of the sales office.

Chrome Oxide

From PVC/1 pigments Technical Committee the following publication is now available: BS318 1988 "Specification for chrome oxide green pigments for paints". This updates the previous standard published in 1968 and is identical with ISO 4621.

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Water based protective coatings with phosphate pigments

by A Bittner, Heubach GmbH & CoKG, Postfach 1160, Heubachstraße, D3394 Langelsheim, West Germany

Abstract

The performances of water based epoxy coatings are optimised by variation of the formulation composition. The study is concerned with the effect of the salt spray and humidity tests. The results of the accelerated tests are mainly influenced by the anticorrosive pigment, the fillers and the ratio PVC/CPVC = Q-value of 0.5 to 0.7. The new formulations of water based primers based on our research are as good as those obtained with conventional solvent-containing epoxy coatings.

1. Introduction

In recent years, legislation relating to the environment in Europe has restricted the use of solvents in coatings. At present, paint manufacturers are attempting to develop coatings of low solvent content. One of the ways of doing this is to use water. According to investigations made by Berger¹, water based epoxy resins are suitable as binders for protective coatings which can be subjected to particularly high demands in aggressive industrial atmospheres.

The present study was carried out to determine to what extent anticorrosive pigments and fillers influence the corrosion protection of water based two component epoxy coatings. To increase the information value of short term tests a simultaneous test was made of conventional solvent-containing epoxy coatings for which practical experience values are available. In practice primers of this type are finished with aliphatic polyurethane top coats and for this reason all the samples were also tested in two coat form.

2. Background

Low molecular liquid resins or

resin dispersions of the known epoxy resins based on bisphenol A and epichlorohydrin can be used as binders for protective coatings. As hardeners, polyamidoamines or polyamine adducts are used, which are made water thinnable to a greater or lesser extent by modification.

In preliminary tests we found that coatings based on epoxy dispersions have inferior anticorrosion properties than coatings based on low molecular epoxy resins. Therefore we used as a binder in our tests, low molecular liquid epoxy with polyamine adduct as a hardener.

The key data of the binders are described in the Appendix. Our tests were carried out with an equivalent ratio of epoxy to hardener because it has been found by Berger¹ that the nature of the hardener has a greater influence on the corrosion protection than the use of too much or too little hardener. The comparative tests of the different pigments and fillers was carried out in accordance with criteria which have been described several times², i.e. the defining of the volume ratios of anticorrosive pigments and fillers, determination of the CPVC by the oil absorption method and fixing of the ratio Q = PVC/CPVC.

For the short-time investigations in the salt spray test according to DIN 50021 and humidity test according to DIN 50017, the objective was to obtain dry film thicknesses of 70 µm in one operation. The finish lacquer or top coat was also applied in a thickness of 70 µm. These dry film thicknesses are necessary on the basis of experience obtained by practical

workers³. The coatings were stored at 7-14 days at room-temperature and thereafter weathered.

3. Influence of the substrate on the results of the salt spray and humidity test

Under the conditions explained above various anticorrosive pigments with talc, titanium dioxide, yellow iron oxide were weathered in accelerated tests on two different substrates.

The results of the salt spray test and the humidity test are shown in Table 1. The overall ratings are derived from the rating criteria of blistering, underrusting and undercutting at the scribe, which were assigned to the respective ratings in accordance with a defined scheme i.e. 100 – best value, 0 – poorest value².

Generally, better results were achieved on grit-blasted steel. In the salt spray test, fundamentally higher blistering, more pronounced underrusting and undercutting at the scribe were to be observed on deep drawn steel. The occurrence of blistering is appreciably higher in the humidity test. See Table 1 and Figure 1.

In Table 2 the salt spray test results of zinc chromate and zinc aluminium phosphate (ZPA) are broken down as an example. With zinc chromate, on deep drawn steel greater blistering and greater undercutting were observed whilst ZPA is equally good on both substrates.

The most pronounced difference is to be observed as regards to the wet adhesion. After exposure in the short-term test all the primers exhibit good wet adhesion on grit-blasted steel⁴ whilst the primers on deep drawn steel are very unsatisfactory independent of the anticorrosive pigment.

ZPA is the most suitable of the tested anticorrosive pigments. On deep drawn steel ZPA is comparable to zinc chromate as regards underrusting and undercutting at the scribe (Figure 2).

Table 1.

Results on degreased deep drawn steel and sand blasted steel

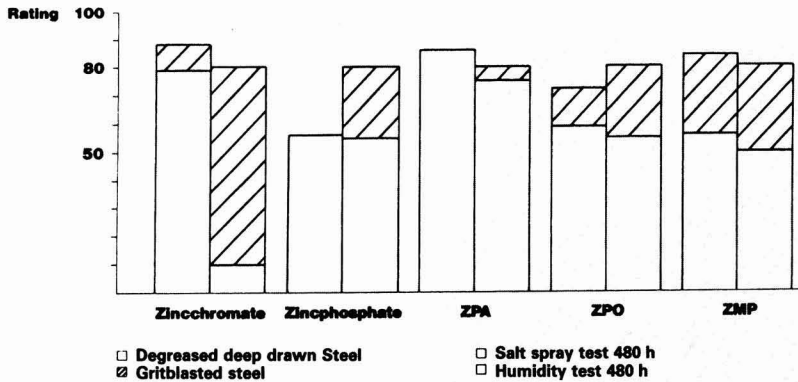
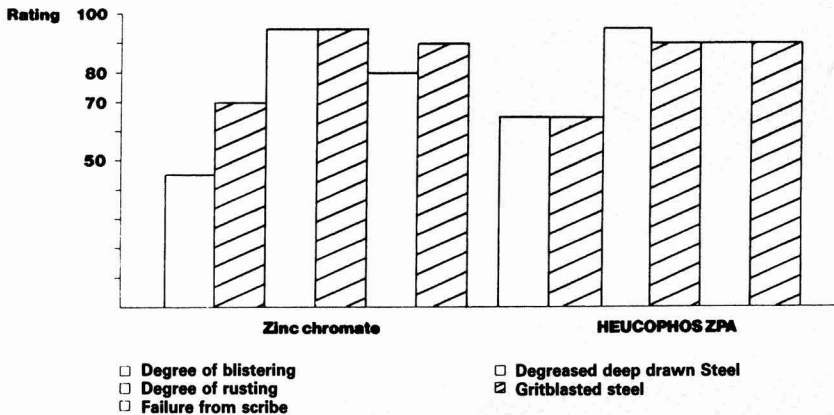


Table 2.

Salt spray test results of zinc chromate and Heucophos ZPA



In the further description of the tests only the results on deep drawn steel are enumerated so as to deal with the more critical substrate from the start.

4. Influence of the pigment/binder ratio (Q-value) on the results of the salt spray and humidity test

As we have seen in earlier investigations the results of accelerated tests are decisively influenced by the pigment/binder ratio⁵. With the anticorrosive pigments ZPA and zinc phosphate the objective was to investigate how water based epoxy coatings behave at different Q-value respective PVC-values. Accelerated tests were carried out at Q-values of 0.5-0.8 with a pigment-filler mixture of

40% by volume titanium dioxide, 25% by volume talc and the balance yellow iron oxide.

Figures 2 and 3 illustrated the results of the salt spray and humidity tests after 480 hours. The protection decreases with both anticorrosive pigments at Q-values above 0.8 in the salt spray test. The blistering is priority evaluated in the humidity test. At Q-values of 0.5 to 0.7 the blistering is the same.

Our results showed that Q-values 0.6 to 0.7 are the optimum values for water based epoxy coatings. In further tests with ZPA we were able to establish that the optimum of anticorrosive pigment is 30-40% by volume. All results obtained so far

are largely consistent with our technical experience gathered with solvent-containing coatings.

5. Influence of the fillers on the results of the salt spray test and humidity test

Further investigations were made with different filler combinations in ZPA-containing coatings.

In a basic formulation of 30% by volume ZPA, 45% by volume titanium dioxide and yellow iron oxide and 25% by volume talc; the talc component was replaced by other fillers (Q-value = 0.5).

In Figure 5 the salt spray test and humidity test results are summarised for lamellar fillers such

Figure 1.
Influence of the substrate on the anticorrosive properties.

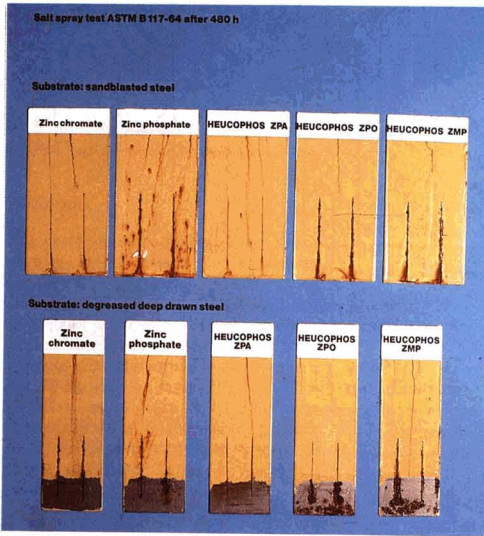


Figure 2.
Salt spray test results of water-based two-pack epoxy primer coatings with various anticorrosive pigments.

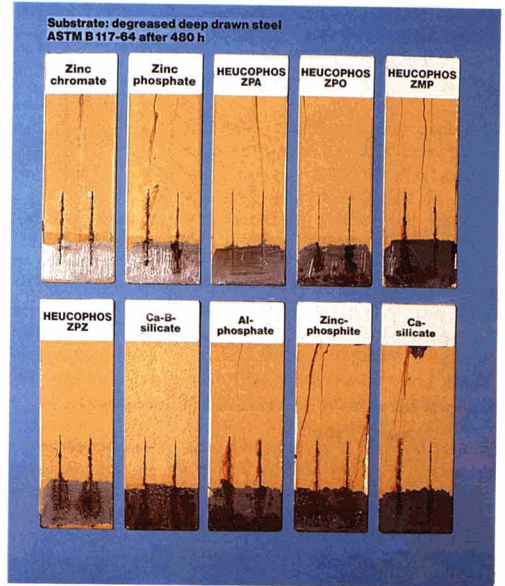


Figure 3.
Influence of PVC-values on the anticorrosive properties (Heucophos ZPA).

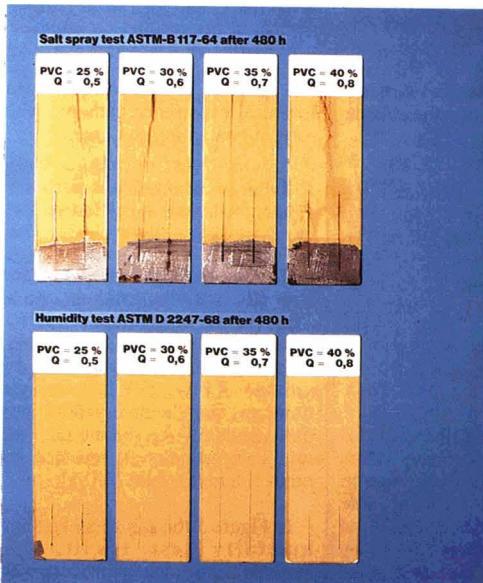


Figure 4.
Influence of the PVC-values on the anticorrosive properties (Zinc phosphate).

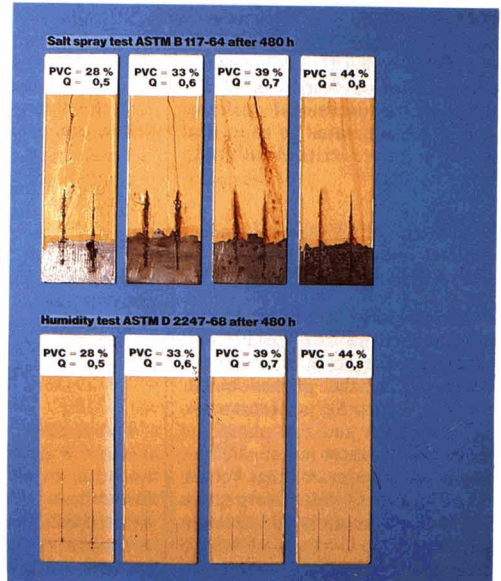


Figure 5.
Influence of different fillers (Silicates) on the anticorrosive properties (Heucophos ZPA).

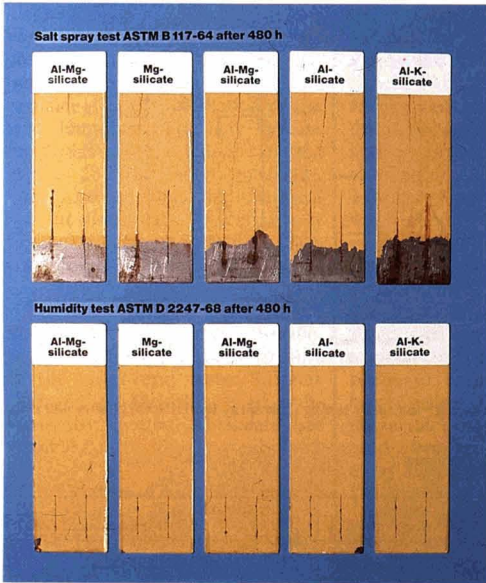


Figure 6.
Influence of different fillers on the anticorrosive properties (Heucophos ZPA).

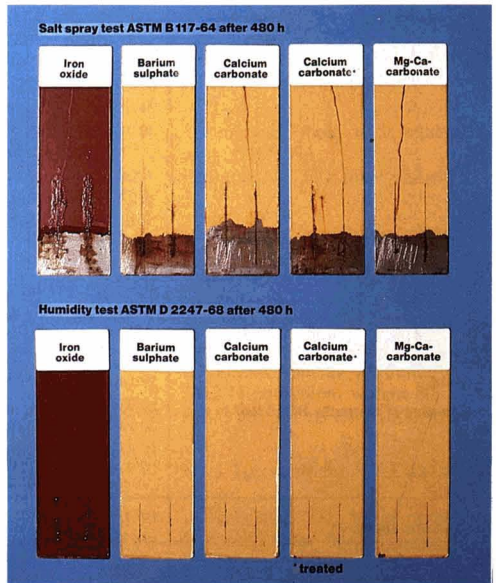
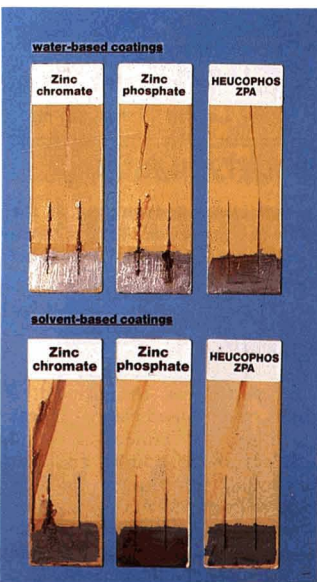


Figure 7.
Comparison of salt spray test results of water-based and solvent-based two pack epoxy primer coatings after 480h. Substrate: degreased deep drawn steel.



as Al-Mg-, or Mg- and Al-silicates. Aluminium-magnesium silicates exhibit very good resistance in the salt spray test whilst aluminium potassium silicates deteriorate appreciably.

Figure 6 shows the results using fillers with a spherical particle structure such as barium sulphate, calcium carbonate and calcium-magnesium carbonate. In the salt spray test the carbonates are comparable to the results of the silicates. In the humidity test these fillers lead to greater blistering. A summary of these results are presented in Table 3.

The fillers tested each have a different oil demand which in our pigment mixtures manifested themselves by the CPVC of the silicates being 10-20% lower than that of the fillers with a spherical structure. Since the ratio PVC/CPVC is constant, the different binder requirement is therefore taken into account and comparability is thus ensured.

Table 3 illustrated the results of the salt spray and humidity tests for

the different fillers. The silicates, such as aluminium-magnesium and aluminium silicate (subsequently treated, pH7) are most suitable because both tests show good values. Although calcium carbonates increase the salt spray resistance they tend to increase blistering in the humidity test.

6. Salt spray tests results with top coat

The various primers were also coated with top coats based on polyisocyanate cured acrylic resin before being submitted to the salt spray test DIN 50021.

The evaluation was made after 480 hours on degreased deep drawn steel and on grit-blasted steel after 720 hours.

The rating of the tests is mainly due to the undercutting at the scribe in accordance to DIN 53167. In general the undercutting at the scribe of all panels was clearly worse on degreased deep drawn steel than on grit-blasted steel. The rating in Table 4 of more than 20 mm means the complete sub-

Table 3.

Results of salt spray and humidity test after 480 h

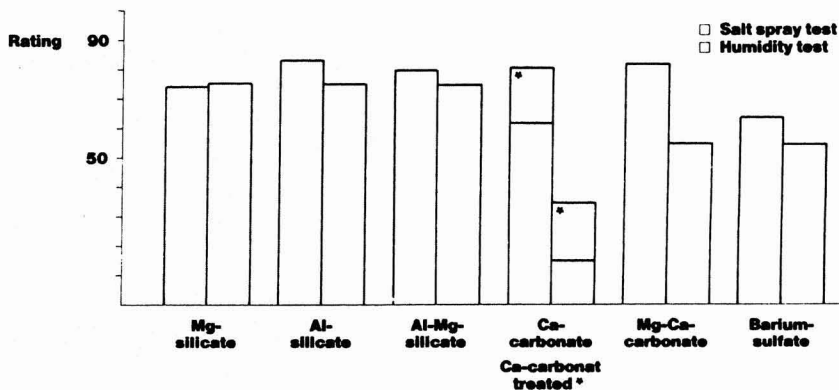


Table 4

Undercutting at the scribe DIN 53167 in mm of epoxy primers with top coats after salt spray testing (Salt spray test DIN 50021 after 480 resp. 720 h)

Water based epoxy primers

Anticorrosive pigment	Q-value	Substrate	
		deep drawn steel (480 h)	grit-blasted steel (720 h)
Zinc chromate	0.7	<20	3-4
ZPA	0.5	5-9	5-7
ZPA	0.6	>20	3-4
ZPA	0.7	>20	4
ZPA	0.8	>10	3-5
Zinc phosphate	0.5	>20	20-25
Zinc phosphate	0.6	>20	7-8
Zinc phosphate	0.7	5*	7-8
Zinc phosphate	0.8	>20	6-8

Solvent-containing primers

Zinc chromate	0.7	3-4	0
ZPA	0.7	0	0‡
Zinc phosphate	0.7	2†	0‡

* Dense blistering, † Poor adhesion, ‡ Partly blistering at the scribe

surface migration of the coatings.

The undercutting on the deep drawn steel surfaces are not influenced by variation of the formulations like different Q-values or different fillers. Important is the use of an anticorrosive pigment. ZPA avoids the loss of adhesion at the scribe on deep drawn steel as well as on grit-blasted steel.

7. Comparison of the results of solvent-containing and water based epoxy coatings

In conclusion, a comparison will

be made between solvent and water based coatings. Key data of the binders are given in the Appendix.

The salt spray tests of the primers on deep drawn steel with anticorrosive pigments like zinc chromate, zinc phosphate and ZPA showed very similar results to the water based and solvent containing epoxy coatings (Figure 7).

The solvent containing epoxy primers are slightly better in the humidity test because of the lower blistering. The solvent containing epoxy primers with top coats also

showed lower undercutting at the scribe in comparison to water based epoxy primers in general (See Table 4).

8. Summary

As shown by the presented results, water based epoxy coatings based on low molecular liquid resin/polyamine adduct hardener with specific formulations can show equal performances to solvent containing coatings. The conclusion relates to the accelerated tests like the salt spray and the humidity test.

As an anticorrosive pigment ZPA has been found to be particularly suitable in water based epoxy primers. This has been found already in conventional solvent based systems compared to zinc chromate and zinc phosphate. Its better protective properties can be explained by the interaction of the zinc-aluminium phosphate hydrate molecules with the binder-carboxyl groups and the metal substrates. One assumes that the chemical modification leads to definitively relative solubilities improving their corrosion inhibitive effect.

The correct choice of the fillers makes it possible to considerably reduce blistering and underrusting in the short-term tests. Silicates such as Al-Mg-silicate or subsequently treated Al-silicate are suitable.

PVC-values of 30-35% by volume respectively. Q-values of 0.6 to 0.7 should be employed as a guideline for the pigment/binder ratio by using ZPA.

The poor wet adhesion of solvent-containing conventional epoxy coatings and water based epoxy coatings to deep drawn steel is a specific phenomenon and is not influenced in our tests by the anticorrosive pigments.

9. Appendix

9.1 Formulation guideline

In the test it proved useful to

disperse the pigments and fillers into the hardener. Stability tests of polyamine adducts of different raw material producers have shown that the viscosity is influenced by various anticorrosive pigments. Zinc phosphate and modified phosphate based pigments do not reduce the stability. Nevertheless the storage stability with different anticorrosive pigments has to be checked in each individual case. It was found advantageous to dilute the polyamine adduct hardener with water in ratio 1:0.8, to add about 4% 1-Methoxy propanol and defoamer and to grind the pigment and fillers as usual. The mill base should have as far as possible the same viscosity as the supplied epoxy resins to ensure the best mixing before using. In the tests polyurethane thickeners up to 0.5% were used to prevent sagging at vertical areas during application.

With a spray viscosity of about 40 seconds according to 4 DIN 53211 it was possible without any trouble in applying the material to test panels using a spray gun. The coatings thus obtained exhibit no flash rusting and have surfaces without craters and pores. They correspond to the quality standard of solvent-containing coatings.

It is difficult to detect any determination of the pot life because the end of the working time is not indicated by any gelling or solvent separation with water based epoxy coating. Since according to the epoxy resin manufacturer a pot life

of 1-2 hours is given precautions were taken of always working the samples within 1 hour.

9.2 Key data of binders used in tests

9.2.1 Water based coatings

Eurepox 776 Epoxide equivalent weight 185-196
Euredur XE 36 Amine value 210

9.2.2 Solvent containing coatings

Beckopox EP 301 Epoxide equivalent weight 450-525
Beckopox EP 116 Epoxide equivalent weight 175-185
Beckopox-Special hardener VEH 2312 H-equivalent weight 80
Ratio EP 301 to EP 116: 1 to 1.

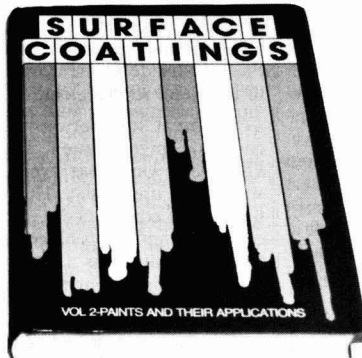
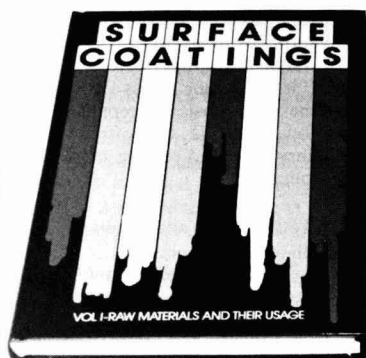
9.2.3 Top coats for 9.2.1 and 9.2.2

Macrynal SM 500 Acryl resin Hydroxyl value 80
Desmodur N Polyisocyanate

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Tolerant coatings

In rust we trust

by Barry Windsor FTSC, AMICorrST, Technical Manager, Corroless International Ltd, Berk House, Basing View, Basingstoke, Hants, RG21 2HW, UK

The word "tolerant" is in many ways much abused. One often encounters the term "tolerant" in relation to surface coatings which are required to perform satisfactorily in aggressive and challenging environments. Of course, it is not just the environment which can be aggressive. In many ways it begins with the quality of the substrate and the challenges associated with application methods, conditions and applicator skill.

On a historical note one should examine the demise of what has often been regarded as the most tolerant coating system, Red Lead. We still hear the cry "There has been no coating to replace Red Lead" which of course, had to be Red Lead primer to BS 2523, Type B. Whilst I would take issue with the former part of the statement, I would certainly agree that the British Standard type was really the only viable type of Red Lead primer with a proven track record. Usage, manufacture and supply of Red Lead primers based on Chlorinated Rubber, Epoxy and relatively short oil length media were unsatisfactory, their performance being significantly inferior to the 2523 type coatings.

With the demise of Red Lead the trend was almost exclusively to Zinc, although it is worthy of mention that Lead Cyanamide primers and Metallic Lead primers had a place in the anti-corrosive priming field for a number of years. The mechanism by which Metallic Lead was effective as an anti-corrosive primer was often regarded at best as controversial, and at worst as a mystery.

As stated the trend towards Zinc concentrated on two favourite pigments both of which were Zinc

Chromates. Zinc Tetroxychromate used then and today as a time proven anti-corrosive pigment in two pack acid containing pre-treatment primers for non-ferrous metals and Zinc Potassium Chromate, used widely and for a long period as the active pigment in anti-corrosive priming systems.

Its proven solubility was both a blessing and a curse. Solubility helped to prove the mechanism by which the pigment was effective, but primers of this type could be prone to blistering under certain conditions. The basic colour—yellow—and its relative lack of opacity was not widely accepted and therefore one often encountered primers of this type with added Iron Oxide pigmentation. In writing of blistering we should also mention Aluminium primers because along with the blistering phenomena and the problems experienced with inter-coat adhesion, Aluminium primers came and went.

Red Oxide has been mentioned as a pigment, and it might be said with the benefit of hindsight that the paint industry that supplied Red Oxide priming paints could be criticised for a low technology approach to anti-corrosion problems, although the die-hards would perhaps stress the quality of the Red Oxide pigment in relation to the water soluble content!

The great leap forward in anti-corrosion pigmentation was Zinc Phosphate which has been and is still widely used today. How and if it works is controversial, but most coating technologists agree that it is the right shape, has a fine particle size and in acidic environments has limited solubility.

We must not forget Zinc rich paints, with 92% Zinc pigmentation

by weight in the dry film, the very high standard of surface preparation required to achieve adhesion and the necessary electrical contacts between particles and the substrate.

Zinc rich paints cannot be regarded as tolerant primers and whilst they have been proven many times as excellent anti-corrosive primers when applied in carefully-controlled conditions with the necessary high substrate standard, they also have problems with chemical resistance, overcoating and when subjected to welding.

In this brief historical review I have attempted to illustrate the changes and trends since the demise of Red Lead and I apologise for not mentioning the 1001 chromates, Borates, Molybdates etc. which have all featured as potential anti-corrosive pigments in surface coatings. I would also suggest that the primary methods put forward by the coatings industry in relation to the protection of metal have all relied on pigments that require at best abrasive blasting to SA2/3 or as a minimum bright metal or metal that has been chemically pre-treated.

I would claim that in recent times the only answer put forward by the coatings industry with regard to coating corroded metal is the anti-corrosion concept known worldwide as Corroless. This concept was originally formulated in the late 1940's and consisted of a special inorganic, lead free anti-corrosion pigment combined with various media that were modified in relation to surface tolerance. It surprises many that Corroless rust stabilising primers were available in Europe as long ago as 1955 and that the same basic concept is with us today and is still offered as an answer to the coating of corroded metal.

Test methods and results

The term stabilisation of rust has been chosen to summarize the various effects of the Corroless System. The structure of a protective film containing

magnetite, as is formed by this System, differs considerable from that of millscale. As the formation of the film does not require high temperatures, it will not lead to the appearance of layers of FeO or to cracking. The film is formed from basic existing rust and as its lattice constant is similar to that of iron, it firmly adheres to the crystal lattice with which it forms an inseparable unity. It is due to this fact as well as to the homogeneity of the film that underrusting caused by external influences is rendered impossible.

An official European institute tested this System, using the definitions of rust given in the Swedish standard SIS 05 59 00 as their base. For testing, panels were used which had been pre-rusted according to rust grade C. After removal of loose rust, two coats of the System primer were applied in the accepted manner. According to the Swedish Standards SIS 05 59 00 rust grade C corresponds to a metal surface from which millscale has almost completely been removed by weathering, i.e. a rusted surface consisting almost 100% of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

Test plates prerusted in this manner and primed with the System were stored at room temperature for 12 months. At the end of this period the paint film was removed with methylene chloride and a black intermediate layer between the paint and the metal surface was exposed. An examination of this layer, by X-ray diffraction using mono-chromatized $\text{FeK}\alpha$ radiation showed that apart from negligible traces of Fe_3O_4 and FeO this layer contained dominating quantities of Fe_3O_4 (Magnetite).

It was, of course, desirable to obtain data regarding the rate at which rust is converted into stable iron oxides. An answer to this question is provided by a highly detailed test conducted by the X-ray diffraction laboratory of a National Commission of Atomic Energy. Metal plates of the size $10 \times 10 \times 1$ cm were used in the test. The use of a plate 1 cm in thickness enabled the laboratory staff to test under conditions which, as far as

possible, approximated those prevailing in actual practice. This would not be the case with thin plates which are normally used for the testing of paints in laboratories.

After the removal of the loose rust the System primers were applied by brush over the remaining layer of basic rust at intervals of 24 hours. Prior to the application of the primers, a sample of rust was taken consisting chiefly of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ or FeOOH .

After paint application one plate was constantly kept at a temperature of 60°C whereas the other one was kept at room temperature (20°C). After removal of the System film with trichloroethylene, at intervals of one month, the oxide film on the metal surface underneath the paint film was subjected to an X-ray diffraction test using $\text{K}\alpha$ cobalt radiation.

At the end of the first month after painting, a test on both plates revealed only $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ i.e. a layer consisting almost exclusively of rust. At the end of the second and third months, apart from $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ small amounts of Fe_2O_3 appeared, in addition to small amounts of Fe_3O_4 which were also distinguished at the end of the fourth month.

The transformation of rust into stable oxides became clearly noticeable at the end of the fourth month and on the plates kept at a temperature of 60°C the stabilization of the former rust into 50% Fe_3O_4 (Magnetite) and 50% Fe_2O_3 (Haematite) was complete after five months. Since Haematite is practically insoluble in acids, the corrosion resistance of a protective film consisting of minerals (iron ore), such as this one is self explanatory. It is obvious that such a protective effect can never be achieved simply by adding Fe_2O_3 or Fe_3O_4 as a pigment to the paint, as contrary to the protective film formed by the System, such coats lack firm adhesion to the substrate.

When, after five months, the protective film has developed

consisting of 50% Fe_3O_4 and 50% Fe_2O_3 , the process of stabilisation has not yet come to an end, but goes on progressing. Later examinations after six months, of the test panels kept at a constant temperature of 60°C showed a magnetite content of 60% and a haematite content of 40%. This, after seven months had increased to 65% magnetite and 35% haematite, and eventually 75% magnetite and 25% haematite after eight months.

After a period of four months, the second plate kept at a room temperature of 20°C showed results similar to those achieved with the plate stored at a constant temperature. On this plate too stabilization was complete (100%) after five months with a rate of 25% magnetite and 75% haematite. Obviously at normal temperatures the process of stabilization takes longer than at elevated temperatures. After a period of eight months, in this case too, the protective film consisted of 65% magnetite and 35% haematite.

The electro-chemical protective effect of the System was furthermore confirmed by a galvanic test conducted in accordance with the specifications of the international Nickel Co, USA. Part of the System paint film was removed from the test plate. The area exposed was dark in colour. Along the edges the plates were covered with a plastic material to protect them against the effects of accelerated galvanic corrosion caused by the method of testing. The test plate was then connected to a copper plate and immersed into an electrolyte consisting of a solution of sodium chloride, using potassium ferricyanide and phenolphthalein as indicators.

As the potential of copper is much higher than that of iron the process of corrosion can easily be recognised by the blue colour which reveals the outflow of ferrous ions. This is the well known "Reaction of Berlin Blue".

However, on the exposed surface area of the System plate a red coloration appeared indicating that

Protective coatings in the process and food industries

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In countless instances, process, works and maintenance engineers face the need for protection of mild steel and concrete plant by the use of a coating. The need may be either against corrosion from the product therein or to ensure that the product itself is kept free from contamination by impurities. There is a wide choice of coatings available for the Food and Process Industries and it is important to categorise them to see how they fit into the broad spectrum of available products.

Coatings are usually defined as corrosion resistant layers of polymeric organic material having thicknesses from 0.125 mm (0.005 in.) to 0.5 mm (0.020 in.) in contrast to linings which can be considered as anti-corrosion

Continued from p.104

the reaction was alkaline, thus proving clearly a transformation of the anodic polarity into a cathodic one. This is proof of the fact that the stabilization brought about by the System will insulate the metal against electro-chemical corrosion.

We hope that the above test data has clearly shown the historical work carried out in proving the original Corroless concept of rust stabilization. Future projects being undertaken at Corroless International include the continual development of new products to combat the problem of corrosion, our latest being the introduction of Corroguard, a range of high performance, glass reinforced coatings which have the ability to stabilise existing corrosion and provide complete protection in areas subject to heavy moisture or immersion i.e. Ballast tanks, mines, gas works, chemical plant and marine structures. ■

barriers of about 0.5 mm (0.020 in.) thickness and upwards.

The selection of the protective coating system primarily depends on the anticipated service conditions, which may vary from mild food quality liquids to strong acid or alkali with organic solvents. Temperatures may range from freezing point to well above 100°C and under severe abrasive or eroding conditions.

Where alternative systems are available, the economics of each one should be evaluated or compared. The ultimate cost is obviously based on the expected service life — low initial cost does not necessarily assure the purchaser a bargain.

Before the actual choice of coatings is made, the specialist contractor requires to know from the client certain basic information. It is worthwhile detailing this 'check list', which is specific for a vessel but can be used for other items of equipment.

1. Size of the vessel to be protected, whether it can be transported to contractors plant or work is to be carried out insitu.

2. Construction of the vessel. If concrete, whether damp or contaminated or suffering from surface laitence. If below ground, ensure vessel is tanked out and free from back water pressure. In the case of mild steel tanks the internal surface should be checked if smooth and free from imperfections, the condition of the welds, whether lapped or rivetted plates, the number of outlets and the ease of manway access. If the vessel has been previously lined, details are required where possible. In the case of oil tanks special cleaning is

necessary before any protective system can be applied.

3. Location. In the case of a fire hazard area special equipment will be necessary, this also will apply to cold rooms in the Food Industry. The distance of the nearest power supply should be noted.

4. Nature of contents. The pH or strength of the solution should be known, and in the case of mixed solutions, all the constituents detailed. This is particularly important in the case of acid solvent mixtures where the solvent may float to the surface and attack the wind and water line.

5. Temperature. Normal operating and any maximum cycling conditions. If vessel is heated, check method used, e.g. coils, live steam etc.

6. Mechanical damage or abrasive conditions. Note the possibility of these occurring as some form of protection or sacrificial lining may be necessary.

7. Cleaning. The method of cleaning the vessel in between batches should be known. This is important in the case of food industry and brewing tanks where sometimes specialised cleaning and sterilizing agents are used.

Having considered all the necessary physical and chemical requirements of the vessel to be protected, one can now examine some of the choices of coatings available.

Phenol Formaldehyde Resins

One of the oldest synthetic plastics used as a coating in the prevention of corrosion to metal is Phenol Formaldehyde resin. The generic term used for these resins is Phenolic. The cured phenolic coating is resistant to a wide range of chemicals which include many acids and solvents. The phenolic coating is usually applied as a spray multi-coat, heat cured system on to freshly grit blasted metal.

Because of the danger of cracking within thick films, which is inherent

in this type of plastic application, coatings are rarely applied at thicknesses greater than 0.25 mm (0.010 in.). It is also advisable to 'inter bake' during the application of the coating to ensure that solvent is not trapped in the coating or that blisters are formed during the final heat treatment of the coating. For this type of coating the applicator must have facilities to grit blast the item to a high degree of cleanliness, ovens to heat it up to 150°C and handling facilities to move it many times during its processing. It is equally true that the item to be coated must also be able to withstand this handling.

Because of the thinness of the coating there is a limit to the mechanical abuse it will withstand. The coating also has an upper temperature limit under immersed conditions of 100°C. This limit can vary for different chemical and mechanical conditions. Continual high temperatures can embrittle the coating and liquid environments tend to have lower maximum temperature limits than gases or solids. When these facts have been borne in mind, Phenolic resin coatings have been successfully used to protect mild steel equipment for over forty years.

Historically, Phenolic coatings have been used as an alternative to glass lined vessels and equipment in the Brewing Industry. The non-tainting properties of the coating is used extensively in the Food Industry to provide sterile coatings for storage vessels, boiling vats, moulds and filters. The good solvent resistance of phenolic coatings is used in the Pharmaceutical Industry where many reactions and intermediate compounds have aggressive solvent conditions and the phenolic coating is again used for storage and reaction vessels. The alcohol content in many spirits can be very high and phenolic coatings have been successfully used in storage vessels for gin and vodka.

Epoxy Resins

Epoxy or Epoxide is the generic term used for plastic materials which formed from epichlor-

hydrin-bis-phenol resins. These resins are able to react with a number of chemicals normally called hardeners or curing agents so that a variety of "Epoxy" are possible.

The properties of the epoxy coating are primarily dependent on the curing agent used. The common early coatings were based on solid epoxy resins and aliphatic amine curing agents. Of necessity these were solvent borne coatings so that their application was by multi-coat spraying. They cure at room temperature so that sophisticated ovens are not required. Care is still necessary during application to ensure that solvents are not trapped within the cured coating. This is achieved by allowing a given minimum time to elapse between coats at a given minimum temperature. Although these coatings cure at room temperature they often require many days to reach their optimum chemical and physical properties. With some innovations these coatings are still successfully being used.

The requirement of economy and speed in the process and food industries has caused the applicator and resin manufacturer to examine the initial epoxy coatings and try to meet market forces. Different resin systems were used and ways were found to reduce the solvent content of the coating formulations so that thicker coats could be applied — resulting in less coats being applied to achieve the same coating thickness. Formulations are now available with less than 20 per cent solvent that can be applied using conventional spray techniques which produce coatings four times thicker than was practical with the initial epoxy coatings. To obtain specific properties these High Build Epoxies often contain other resinous materials. The most common type is the Coal Tar Epoxy. These systems can be applied at thicknesses of 0.25 mm (0.010 in.) per coat.

The ultimate epoxy system to be formulated is the solvent-free epoxy coating. This uses liquid epoxy resins and liquid polyamine or polyamide curing agents. The

limiting factor concerning the film thickness of these coatings is the 'sagging' characteristics of the formulation. It is possible to successfully apply some formulations thicker than 0.5 mm (0.020 in.) in one coat. The equipment required to apply solvent-free epoxy coatings has been quite complex.

This is because although the components are liquid, they are very viscous, the basic epoxy resin has a viscosity of approximately 130 poise at room temperature. Spray equipment is available to apply solvent-free epoxy coatings which utilise heating, measuring, high pressures and mixing. Development is continuing to try and simplify the apparatus required to apply these types of coatings.

The surface to which epoxy coatings are applied are varied, from aluminium to wood. The methods of surface preparation are equally as varied, but they are all aimed at achieving the same result — a clean and sound substrate. The two main surfaces coated are mild steel and concrete. Mild steel surfaces are adequately cleaned by grit blasting. For items where it is not possible to coat within 4 hours of cleaning it is good practice to apply a 'holding primer'. The method of cleaning concrete depends very much on the contamination, and it is not possible to generalise. An important feature of coating concrete is to ensure that the surface is sound. This often means the removal of a laitence which requires care, as the concrete surface may be damaged during this operation causing large irregularities in the concrete surface which may be difficult to adequately coat.

Having a choice of curing agents means that it is possible to produce epoxy coatings with differing chemical and physical properties. This is utilised in formulating coatings which can be applied at high and low ambient temperatures, at differing atmospheric relative humidity and to damp surfaces. Within these variations it is possible to generalise on the properties of epoxy coatings. They are resistant to a wide range of

inorganic chemicals and to a more limited range of organic chemicals. The upper temperature limits of the coatings depend on the Heat Distortion Temperature of the cured resin system, these vary between 30°-80°C.

Epoxy coatings, with their range of curing agents and the resulting properties they produce, are used to protect a variety of substrates, in a large variety of environments.

Phenolic/Epoxy Resins

As mentioned previously, epoxy resins will react with a number of chemicals. One such group of chemicals are phenol formaldehyde resins. The reaction between the two resin types is called a pre-condensation, it entails refluxing and combining the two resin solutions. The resins produced can then be formulated into spray applied coatings. The resulting coatings are sufficiently important for them to warrant a separate section in this review. Phenolic/Epoxy coatings are resistant to a wide range of chemicals which include many inorganic compounds, they can be room temperature curing or heat curing. The heat curing coatings, having the greater chemical resistance. Unlike Phenolic coatings, the Phenolic/Epoxy coatings do not suffer from cracking within thick films. This allows the thickness of the coating to be determined by economics and practice. Generally the coating thickness if 0.3 mm (0.012 in.). This is achieved by multi-coat spray application, relatively high wet film thicknesses can be applied using airless spray equipment. 'Inter bake' procedures are again advisable between coats for the heat curing type whilst the room temperature curing coating requires care during application to ensure that solvents are not trapped within the cured coating. The heat cured coatings are given their 'Final Bake' at temperatures in the region of 200°C. For large structures it is important that the heating schedule is such that all the coating attains this temperature. This is achieved by using gradual temperature rises and regular monitoring using

thermocouples attached to the article.

The Phenolic/Epoxy coatings are able to withstand an increased amount of mechanical abuse compared with the Phenolic coatings. The smooth tough surface produced has been found to considerably increase the life of pipes carrying abrasive slurries as experienced in mines and quarries. With their broad chemical resistance, upper temperature limit of 100°C and sterile surface, the Phenolic/Epoxy coatings are extensively used in the process and food industries.

From fixtures and fittings, through pipes to storage vessels, Phenolic/Epoxy coatings are protecting products from contamination and the fabric from corrosion. Examples of the diversity to which these coatings are put include the relining on site of an originally glass lined condensate return tank running at 90°C and containing up to 10% Sulphuric Acid, site lined storage vessels to hold 'Pot Ale' effluent from a distillery prior to treatment, and lager fermentation and conditioning vessels kept at 2°C.

Polyurethane Resins

Urethane is the chemical name for the reaction product of an isocyanate and hydroxyl group. The polyurethane coatings considered now will be only those which cure by this mechanism. For the coating formulator and applicator there are a number of isocyanate and hydroxyl compounds available and they are able to produce a variety of coatings, comprising of room temperature and heat curing systems, one and two pack systems. When fully cured the polyurethane coating will have good abrasion resistance. Polyurethane coatings can be applied at a variety of thicknesses, from less than 0.025 mm (0.0001 in.) when used as a wood varnish to more than 0.5 mm (0.020 in.) when used as an elastomeric pipe lining. They are also the first coatings reviewed in this Paper which with correct formulation are light stable. Like most plastic, polyurethanes are not

attacked by, and so will not support, bacteria. This property is used in supplying coatings for protecting and decorating the outside of vessels and the inside of buildings especially in the Food Industry.

The choice of which polyurethane systems to use is often governed by application conditions required by the coating. The one pack, room temperature cured system is usually of the moisture curing type. Because of the mechanics of the moisture curing process, these coatings are best applied as thin films, and so are used less where thick coatings are required. Thin film coatings have a use on concrete floors to reduce dusting, assist cleaning and offer some protection against small spillages, which is where one pack room temperature polyurethane systems are often used.

The heat curing polyurethane systems are often used to coat hand tools, used in the process of food industries, where their colour stability, abrasion resistance, flexibility and chemical resistance are fully exploited. The more conventional type of polyurethane coating is produced by the two pack spray applied system. Since the late 1930's when the polyurethane polymer was discovered in Germany, these polyurethane coatings have been improved, tried and tested in a number of applications, from protecting the fuel hold on minesweepers, which in some cases were also the hull, to the external coatings of aircraft. The substrates to which they can be applied are varied. On porous surfaces adhesion is aided by the coating penetrating into the substrate and forming a 'key'. On metal surfaces adhesion is aided by using primers. As always the best results are obtained when the coating is applied to clean surfaces. An extra hazard incurred during the application of polyurethane coatings is that water will react with the coating during its cure, resulting in a coating which differs from that intended. Care is required, especially during site application of vessel coatings to ensure that condensation is not allowed to form

before the coating has cured.

Neoprene Resins

Neoprene is the commercially accepted and recognised name for polychloroprene, and was the first commercially successful synthetic rubber. The types of synthetic rubbers now available is considerable and their use and limitations could easily fill a separate paper. In this review only Neoprenes are chosen because of their historic importance, our own knowledge and the important use to which Neoprenes are put as coatings. Neoprenes tend to be tough coatings with a high degree of elasticity. Coatings are available with tensile strength of 8 MN/m² and an elongation of 500%. The chemical resistance of the Neoprene coating depends on the degree of polymerisation of the Neoprene polymer used.

Generally, they are not recommended for a number of solvents nor strong oxidising agents, but that still leaves a lot of chemicals to which they are resistant.

As a coating material Neoprene is available in a number of forms,

one pack, two pack, room temperature cured and heat cured. The different types and uses to which Neoprenes are put can be used as excellent examples to illustrate some demarcations which occur when thinking about coatings. The one pack material relies greatly on solvent evaporation as its method of cure. The degree of polymerisation of the Neoprene used in these systems is not very large so that the chemical resistance of the coating is not exceptional. The one pack Neoprene systems are, therefore, not used in aggressive chemical conditions. They belong to the 'maintenance' coating category. The 'maintenance' coating category is given to those items of equipment and plant which require some protection, but are not allowed to have sophisticated, expensive coatings which may be over engineered for the limited protection they require. This category includes the outside of storage and process vessels, structures exposed to corrosive gases, fire fighting equipment, machinery. The two pack Neoprene systems rely for their curing on solvent evaporation and vulcanization. This invariably means that

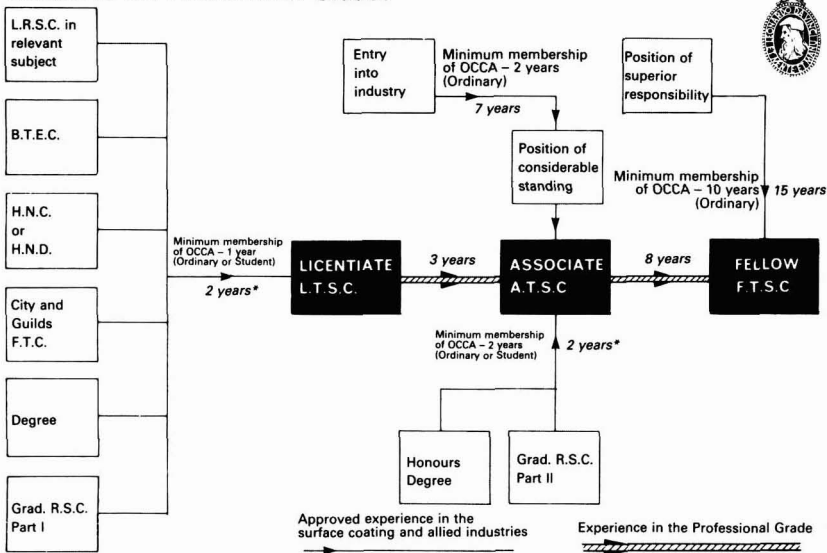
their chemical resistance is increased, as are some of their physical properties. The wide chemical resistance of Neoprene to acids, alkalies and many fuels, coupled with their heat resistance of up to 120°C and their tough resilient physical properties means that they can be used to protect plant and equipment in very aggressive chemical and mechanical conditions.

The Neoprene coatings are solvent borne, so their application is achieved by multi-coat spray, brush or roller. Relatively thick films per application are possible but care is required during the application to ensure that solvent is not trapped in the coating. Neoprene coatings are frequently used for their abrasion resistance, and are often used at large coating thicknesses .75-1.5 mm (0.03-0.060 in.).

These thicknesses cannot be achieved quickly, but require many days processing before the final thickness and chemical resistance is attained. A quick turnround of Neoprene coated equipment is not always possible even when heat cured systems are used. ■

Optional Professional Grade for Ordinary Members

Routes to the Professional Grades



Liquefaction of cellulosic paint thickeners. Part 2: Quantitative aspects of enzymatic degradation

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Summary

A study with microbial isolates showed that fungi (eg. *Cephalosporium sp* and *Fusarium sp*) were able to completely liquefy a range of soluble cellulosic paint thickeners, while spore-forming bacteria (eg. *Bacillus spp*) appeared to be more substrate specific in their action (and generally less severe in effect). Examples of these organisms caused thinning when inoculated into an acrylic emulsion paint (thickened with hydroxy ethyl cellulose), and it was suggested that the behaviour observed could be paralleled in manufacturing situations. A commercial cellulase enzyme was extremely active under the same test conditions and, following some exploratory experiments, this material was utilised in a study to determine enzyme "activity" towards a range of cellulose-ethers. Activities varying from 9-50% of the rated value were obtained, which enabled estimations to be made of significant contamination levels in paint. For example, 10^{-6} - 10^{-5} Enzyme Units/ml paint (equivalent to 0.07-2.27 ppm commercial cellulase) produced a 1 poise loss of low shear viscosity in a selection of emulsion paints, while 2×10^{-6} - 6×10^{-5} Enzyme Units/ml paint (0.14-18.1 ppm) caused 50% loss of initial viscosity in the same paints.

Introduction: Refs. 3, 8, 9, 11, 12

This paper and the earlier part derive from several projects undertaken during 1981-85. Part 1 described work carried out to try to determine the practical importance to the UK/European paint industry of redox and enzymatic thinning processes. It was shown that, while

cellulose-ether solutions suffered degradation from the presence of as little as 10 ppm of certain redox chemicals, the viscosities of a range of emulsion paints thickened with cellulose-ethers were not substantially reduced by an order more of these same agents. By comparison, the majority of the paints showed substantial loss of both low shear and high shear viscosity when contaminated with 1-10 ppm of a commercial cellulase enzyme. Finally, a simple technique was described which showed promise as a means of distinguishing between enzyme and redox contamination in emulsion paint.

The earlier results supported the hypothesis that European paint manufacturers should in the main view microorganisms/microbial enzymes as a greater threat to viscosity stability than contamination by redox chemicals (bearing in mind that an atypically high concentration of the latter could well cause a thinning problem with certain formulations eg. Paint A1 in Part 1). Nevertheless, there remained sufficient uncertainties in the field of biodeterioration of liquid emulsion paints to preclude definitive statements on causative organisms (and, therefore, sources of cellulase enzymes), or on the minimum levels of cellulase contamination which in practice can give liquefaction problems. Thus, the objectives of the work described in Part 2 of the paper were to investigate the thinning action of microorganisms both on cellulose-ether solutions and emulsion paints and, in particular, to try to quantify enzymatic thinning of the latter.

Experimental: Refs. 1, 4, 7-9

Water soluble cellulose-ethers used throughout the study (ie. as solutions and as paint thickeners) were as follows:
Bermocoll E320G - ethyl hydroxy ethyl cellulose (EHEC)
Celacol HPM15000DS - hydroxy propyl methyl cellulose (HPMC)
CMC7M31C - sodium carboxy methyl cellulose (SCMC)
Courlose CP10 - mixed sodium carboxy methyl cellulose/hydroxy propyl methyl cellulose (SCMC/HPMC)
Natrosol 250MR - hydroxy ethyl cellulose (HEC)

Liquefaction by microbiological agents

From the stock cultures held at Paint RA, a group of microbial isolates which had been associated with thinned products were selected for study. In a first experiment, all the organisms were inoculated into a range of media based on 2% HEC in order to assess liquefactive capability. The HEC solutions were made with either distilled water, mineral salts offering nitrate or ammonium sources of nitrogen, or mineral salts/nutrient broth to provide growth factors for fastidious organisms. Incubation was for 8 weeks at either 25 or 30°C, with "side-by-side" comparison with control solutions being used to assess whether liquefaction had occurred. Based on the data obtained, organisms were selected for inoculation into additional cellulose-ether solutions (viz. EHEC, HPMC, SCMC/HPMC) and into acrylic and va/veova emulsion paints thickened with HEC, paint viscosities being monitored on an ICI Rotothinner Viscometer as described in Part 1. A commercial cellulase enzyme (Cx) was included in the same experiments for comparison.

Quantifying enzyme action

Initially, it had been hoped to undertake a quantitative study using cellulase enzymes "generated" in cultures of cellulose-ethers which had been thinned by selected test organisms.

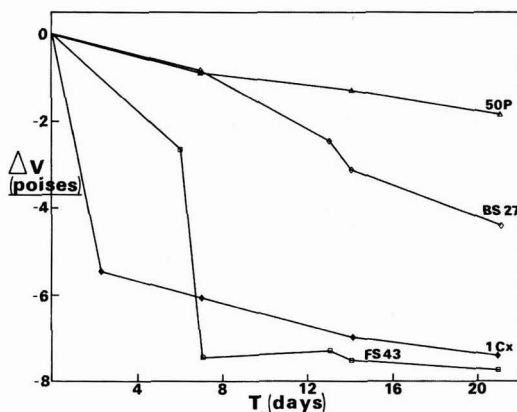
To this end an attempt was made to extract cellulolytic protein from culture media using a scheme of low temperature acetone precipitation described by Sison et al, but this proved unsuccessful in yielding active products. Work was then undertaken in which filter-sterilised thinned culture media were used directly as cellulase sources. These proved able to liquefy fresh cellulose-ether solutions but the relatively high volume addition rates required to introduce sufficient active agent, as well as their variable content of active material, made them unsuitable for use as the basis of a quantitative study.

In the circumstances, a fresh sample of cellulase enzyme (derived from the fungus *Trichoderma viride*) with a known activity of 0.02 Enzyme Units/mg was obtained from BDH Ltd to use for quantitative studies. Enzyme activity is usually determined by assaying glucose production from SCMC at pH5, and it was confirmed that the same result of 0.02 EU/mg could be obtained using the colorimetric method kindly provided by BDH Ltd. However, since emulsion paint systems generally have a pH nearer to 8 and will not only be thickened with SCMC, it was considered necessary to assay cellulase "activity" under these more relevant conditions using both the colorimetric method (as a measure of end-product formation) and the viscosity loss method described in Part 1 (as a measure of cellulose-ether substrate degradation). The additional systems studied were solutions of EHEC, HEC, HPMC, SCMC/HPMC, dissolved in McIlvaine's phosphate buffer to give a pH of 8.

As work progressed it became apparent that the data being generated on cellulase action would benefit from rationalisation, and that enzyme "activity" was a variable parameter which required definition in each cellulose-ether test system. Viscosity loss was (and still is) the problem of concern to the paint industry and this in turn was taken to be a manifestation of the underlying cellulose-ether sub-

Figure 1.

Viscosity loss (ΔV) vs Time (days) for Paint A1 inoculated with 50 ppm potassium persulphate (50P), *Bacillus pumilus* (BS27), *Fusarium sp* (FS43), and 1 ppm cellulase enzyme (1Cx).



strate degradation. Therefore, it was decided to estimate cellulase "activity" in such terms, working first with cellulose-ether solutions and then with emulsion paints thickened with the same materials. All the test cellulose-ethers were dissolved in pH8 buffered solution to give a range of concentrations from 0.5-3.0% w/v, with SCMC also being prepared as a pH5 reference system using acetate buffer. The low shear viscosity of each system was determined as described in Part 1, and viscosity/concentration calibration curves generated.

Fresh 2% w/v solutions of each system were prepared, and these inoculated with filter-sterilised cellulase enzyme solutions at a constant volume addition rate such that a range of enzyme "concentrations" were obtained. Low shear viscosities were determined at intervals over a fairly extended time period (taking all practicable precautions to maintain sterility). It was possible to use the data obtained to assign an "activity" to the enzyme in each of the cellulose-ethers (see Table 3) and to apply this to paints thickened with the same materials. A selection of 6 paints were prepared using a Chemcol-Mischer high speed stirrer, and 150 ml aliquots of these inoculated with filter-sterilised

cellulase enzyme solutions as above to give a range of enzyme "concentrations". Blank controls were obtained by inoculating paints with the same volume of sterile distilled water. As before, low shear viscosities were determined at intervals over an extended time period. It was then possible to estimate the sensitivity of each test paint to enzymatic degradation (see Table 4).

Results and Discussion: Refs. 1, 2, 5, 6, 8-10

Liquefaction by microbiological agents

Representative results showing the action of microbial agents on cellulose-ether solutions are given in Table 1, while Figure 1 shows viscosity changes which occurred when Paint A1 (see Part 1, Table 3) was similarly inoculated.

The organisms in Table 1 belong to 3 groups, namely, aerobic non-sporing bacteria (ie. *Pseudomonas aeruginosa*), aerobic/anaerobic spore-forming bacteria (ie. *Bacillus spp*), and aerobic fungi (ie. *Cephalosporium sp*, *Fusarium sp*). Results obtained in this and other studies suggest the behaviour illustrated to be fairly typical, that is the fungi (and the fungal enzyme Cx) show a general cellulolytic action

towards the cellulose-ethers, the spore-formers show cellulolytic action that tends to be more specific and less severe while *P. aeruginosa*, despite belonging to a frequently isolated genus, rarely appears cellulolytic (although an atypical example has been described). The results obtained with Paint A1 (see Figure 1) suggest an interpretation which may have parallels under manufacturing conditions, namely that the fungus (FS43) developed initially as a surface growth which caused a dramatic viscosity drop only when it was mixed in at day 6 (the first viscosity measurement), while the bacterium (BS27) appeared to provide a more uniform effect perhaps because it was able to act throughout the body of the paint.

Quantifying enzyme action

In Table 2 comparison is made between 2 methods of assessing cellulase activity on cellulose-ethers. According to the glucose assay method, the enzyme showed zero or very low activity in the pH8 systems (NB. a condition chosen to be "representative" of emulsion paints). Nevertheless, viscosity losses observed were generally severe for the same systems. In view of the apparent disparity in results it was decided that a viscosity related method of assessment would provide more useful data.

Figure 2 shows viscosity/concentration curves obtained with SCMC at pH5 (the standard system) and pH8. Although not reproduced here, similar "calibration" curves were generated for the remaining cellulose-ethers at pH8. These curves were used to convert viscosity measurements made on cellulose-ether solutions (to which had been added various levels of cellulase enzyme) into equivalent cellulose-ether loss, when the type of curves shown in Figure 3 were obtained for SCMC/pH5 as well as for the remaining test systems. As can be seen the curves tend to level off at a "maximum cellulose-ether loss" related to a given addition level of cellulase enzyme (eg. in Figure 3)

Table 1
Action of microbial agents on cellulosic paint thickeners

Test Agent	Cellulose Ether Liquefaction			
	HEC	EHEC	HPMC	SCMC/HPMC
<i>Pseudomonas aeruginosa</i> (BS1)	-	-	-	-
<i>Bacillus subtilis</i> (BS21)	+	+	-	+/-
<i>Bacillus pumilus</i> (BS27)	+	-	-	-
<i>Cephalosporium</i> sp (FS29)	+	+	+	+
<i>Fusarium</i> sp (FS43)	+	+	+	+
Cellulase Enzyme (Cx)*	+	+	+	+

Key: + = viscosity loss, - = no thinning observed.

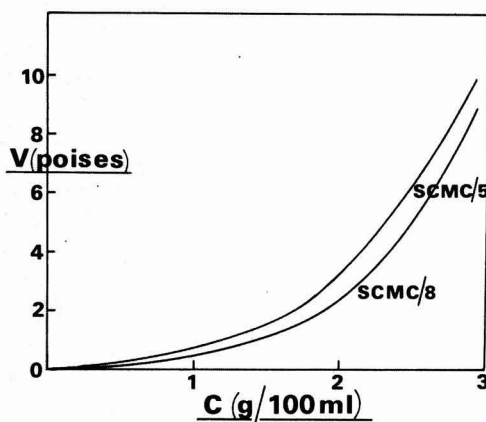
*derived from *Trichoderma viride*, obtained from BDH Ltd.

Table 2
Assessment of cellulase action on paint thickeners by glucose assay and viscosity loss.

Test System	Glucose Assay		Viscosity Loss
	EU/mg	% of standard activity	
SCMC:pH5*	0.022	100	severe
SCMC:pH8	0.001	4.5	severe
EHEC:pH8	0	no activity	severe
HEC:pH8	0.001	4.5	severe
HPMC:pH8	0	no activity	moderate-severe
SCMC/HPMC:pH8	0.001	4.5	severe

*standard system used in assessment of cellulase enzyme activity by glucose assay (the enzyme from BDH Ltd was rated at 0.02 Enzyme Units/mg).

Figure 2.
Viscosity (V) vs concentration (C) for solutions of sodium carboxy methyl cellulose (SCMC) at pH5 and pH8.



the enzyme has been added at levels of 4×10^{-7} - 2×10^{-5} Enzyme Units/ml).

Figure 4 shows maximum cellulose-ether loss plotted against enzyme activity for the full range of test systems, when the series of curves shown has resulted. From these were read off the cellulase enzyme addition levels which caused the same apparent cellulose-ether loss in the different test systems, hence the relative cellulase enzyme "activities" shown in Table 3 were estimated by comparison with the standard system of SCMC at pH5.

The final stage of the work, and primary aim of the study, was to quantify enzymatic degradation of emulsion paints in terms meaningful to the industry. Figure 5 gives examples of the curves obtained from 3 of the 6 test points when "maximum viscosity loss" was plotted against cellulase enzyme activity as discussed previously. The remaining paints yielded equivalent curves. In a similar manner to the earlier cellulose-ether results, from these curves were read off the cellulase enzyme addition levels which caused the same degree of liquefaction in the different paints namely, 1 poise viscosity loss or a loss of 50% initial paint viscosity. Table 4 shows the data obtained in which cellulase addition has been given both as Enzyme Units/ml and as ppm of the commercial product.

Depending upon the purity of this latter material, the concentration of actual enzyme could feasibly be considerably less than the values estimated (which would put "danger levels" for enzyme contamination of cellulosic emulsion paints very much into the sub ppm region).

Conclusions

Tests carried out on solutions of various cellulosic paint thickeners showed that fungal isolates belonging to the genera *Cephalosporium* sp and *Fusarium* sp, as well as a fungal cellulase enzyme, were able to liquefy all types tested. Bacteria belonging to the genus *Bacillus* also

Figure 3.

Equivalent cellulose ether loss (C - E loss) vs Time (T) for sodium carboxy methyl cellulose solution at pH5, with cellulase enzyme addition levels of 4×10^{-7} EU/ml, 2×10^{-6} EU/ml, 4×10^{-6} EU/ml and 2×10^{-5} EU/ml.

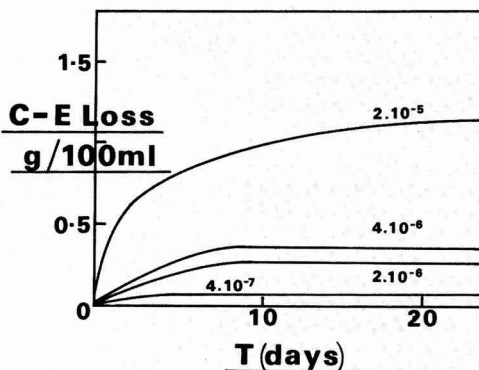


Figure 4.

Maximum cellulose ether loss (Max. C - E loss) vs Cellulase enzyme activity (Cx activity) for sodium carboxy methyl cellulose (SCMC) at pH5 and pH8, and hydroxy ethyl cellulose (HEC) at pH8, ethyl hydroxy ethyl cellulose (EHEC) at pH8, hydroxy propyl methyl cellulose (HPMC) at pH8, and a mixed cellulose (SCMC-HPMC) at pH8.

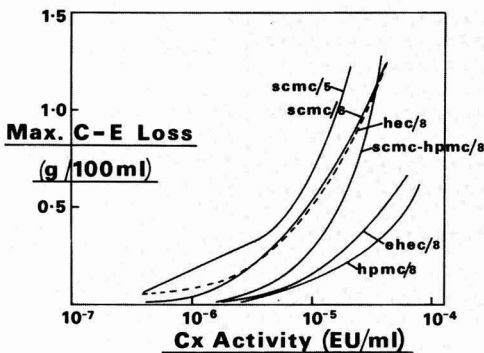
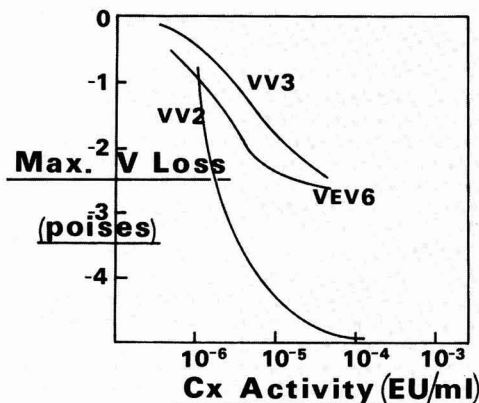


Figure 5.

Maximum viscosity loss (Max. V loss) vs Cellulase enzyme activity (Cx activity) for Paints VV2, VV3 and VEV6.



caused liquefaction but this was less severe and appeared more specific in effect.

The same test organisms (viz. *Bacillus pumilus* and *Fusarium sp*) were able to thin an acyclic emulsion paint, and it was suggested that the behaviour illustrated (in Figure 1) might have practical implications.

Using the viscosity/concentration relationships for a range of cellulose-ethers in solution, it was shown that the "activity" of a commercial cellulase enzyme varied on average from 9-50% of its rated value. This enabled estimations to be made in paints of enzyme contamination levels able to cause, for example, either 1 poise viscosity loss or a loss of 50% initial paint viscosity. Values in the former case were 10^{-6} - 10^{-5} Enzyme Units/ml paint (ie. 0.07-2.27 ppm commercial cellulase), and in the latter case 2×10^{-6} - 10^{-5} Enzyme Units/ml paint (ie. 0.14-18.1 ppm commercial cellulase).

Acknowledgements

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Table 3
Activity of cellulase in terms of equivalent cellulose ether loss

Cellulose Ether Loss (g/100 ml)	Relative Activity of Cellulase (%)				
	SCMC :pH8	HEC :pH8	EHEC :pH8	HPMC :pH8	SCMC/HPMC :pH8
1.17	57	57	—	—	59
0.65	69	64	16	11	45
0.5	72	65	17	11	40
0.36	67	61	17	11	32
0.27	44	43	12	8	20
0.18	32	36	8	7	15
0.1	27	35	7	7	13
0.065	31	40	7	7	13
Average*	50% = 0.01 EU/mg	50% = 0.01 EU/mg	12% = 0.0024 EU/mg	9% = 0.0018 EU/mg	30% = 0.006 EU/mg

*standard system of SCMC:pH5 rates the BDH Ltd Cellulase used in the work as 100% activity = 0.02 Enzyme Units/mg.

Table 4
Sensitivity of test paints to liquefaction by cellulase enzyme

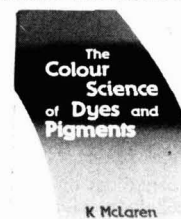
Paint Code*	Type*	1 Poise Vis Loss		50% Viscosity Loss	
		EU/ml paint	ppm	EU/ml paint	ppm
VV2	va/veova:HEC	1×10^{-6}	0.07	2×10^{-6}	0.14
VV3	va/veova:HPMC	3.2×10^{-6}	1.21	1.2×10^{-5}	4.8
VEV6	va/ethylene/vc:EHEC	1×10^{-6}	0.29	3×10^{-6}	0.9
VEV7	va/ethylene/vc:SCMC/HPMC	1×10^{-5}	1.2	6.3×10^{-5}	7.2
A5	acrylic:EHEC	7.9×10^{-6}	2.27	6×10^{-5}	18.1
SA4	styrene acrylate:SCMC/HPMC	5×10^{-6}	0.58	4×10^{-5}	4.6

*formulations given in PRA Technical Report TR/5/85.

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An electrochemical investigation of the effect of the adhesion of a lacquer coating on the underfilm corrosion

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Abstract

Lacquer-coated mild steel electrodes with concentrically-divided substrates were immersed in aerated 3% sodium chloride solution, and measurements of galvanic current flow and AC impedance taken between different areas of the substrates. Some of the specimens had adherent lacquer coatings, and some had non-adherent coatings.

The beneficial role of adhesion is thought to be in impairing the formation of a layer of electrolyte at the coating-substrate interface, preventing ionic current flow and the spread of corrosion over the surface. It was indicated that other important factors determining the degree of protection given by the coatings were the physical structure of the coating and the ability of chloride ions to diffuse to the substrate surface.

Where a coating blister developed between the two areas of the substrate, AC impedance showed the corrosion processes within the blister to be governed by a diffusion controlled mechanism, related to the diffusion of ionic species, not to the diffusion of oxygen.

Introduction

The work carried out here has been designed as a sequel to previous work by ourselves¹. This concerned the use of a zero resistance ammeter to measure the galvanic current flow between concentrically divided regions of the substrate underneath an artificial blister on a lacquer coated mild steel panel during immersion in sea water solution.

Basically, the flow of galvanic currents was demonstrated, thus showing corrosion underneath a lacquer coating to be electrochemical. Contamination of the blisters with sodium chloride was found to promote a small amount of visible corrosion and current flow during the early stages of immersion, as compared to uncontaminated blisters, where no visible corrosion or current flow was observed in the early stages. However, the contamination did not appear to be a major factor, as much more widespread corrosion and much higher current flow was observed to suddenly initiate underneath both contaminated and uncontaminated blisters. The length of time before this occurred had a direct dependence on the thickness of the lacquer coating, and it was therefore suggested that the corrosion processes were mainly promoted by species diffusing through the lacquer from the external solution. The exhibition of an induction period before the onset of corrosion has also been demonstrated by Zavrzhina et al², and Schober³ and Bellobono et al⁴ have linked the diffusion of chloride ions through a lacquer coating to the substrate with the onset of corrosion.

We decided to investigate the effect of the presence or absence of adhesion between a lacquer coating and a substrate, principally with a view to understanding the influence of adhesion on the corrosion processes and the electrochemical

behaviour, which was far from clear in the light of the experimental findings reported previously. James⁵ suggested blistering was the primary process with corrosion consequent upon it, but Gay⁶ found that corrosion had to occur for blisters to develop to an appreciable size. Garber and Zuev⁷ found an inverse dependence of corrosion on the strength of adhesion of the coating, but Schwenk⁸ and Walker⁹ could find no correlation between corrosion and adhesion.

The idea of our work was to make specimens of mild steel coated with lacquer, some with the lacquer coating adhered to the substrate, and some with the coating not adhered. Similar specimens have been used before by Mikhailovskii et al¹⁰ on magnesium, and by ourselves on mild steel¹¹.

It was planned to make some specimens with concentrically divided substrates, so that the centres could be contaminated with sodium chloride and galvanic current flow and AC impedance measurements taken between the centre and outside of each substrate. This was to investigate the effect of contamination of the substrate in promoting the corrosion processes, particularly regarding osmotic transfer of water through the coating, as proposed by van der Meer-Lerk and Heertjes¹².

Experimental Method

Eight specimens were made with electrically divided substrates, each specimen consisting of a circular central mild steel electrode of diameter 0.3 cm and a mild steel panel surrounding this as an outer electrode, the electrodes being electrically separated with a polytetrafluoroethylene/polyether-sulphone mixture to serve as insulator.

The circular mild steel electrodes were made from mild steel rod supplied by the Chemical Engineering Department, UMIST. Electron probe micro-analysis gave

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the composition of this as being virtually identical to that of the mild steel panels, which were 1.2 mm "Gold Seal" test panels, supplied by Pyrene Chemical Services Ltd. The compositions of the electrodes are shown in Table 1.

Table 1
Electrode compositions

	Mild steel panel	Mild steel rod
Iron	97.85%	97.85%
Manganese	0.43%	0.45%
No other element	>0.1%	

The polytetrafluoroethylene/polyethersulphone mixture was supplied by Imperial Chemical Industries Ltd., and was a solution of polyethersulphone and polytetrafluoroethylene in a mixed solvent system, containing approximately 50% polytetrafluoroethylene.

Each specimen was constructed by drilling a 0.4 cm diameter hole in the centre of a degreased 7.5 cm x 5 cm steel panel, inserting a degreased piece of the mild steel rod in the centre of this, and affixing it in position with epoxy putty adhesive, such that one end of the rod was flush with the surface of the panel, and such that the rod was in the centre of the hole. The space between the rod and panel was filled with polytetrafluoroethylene/polyethersulphone mixture, which was allowed to dry. Then the surface was polished to 1200 grit with carbide paper, cleaned with trichloroethylene and the specimens stored in a desiccator for 1 week.

Each central electrode was contaminated by applying 5 μ l of 0.45g/l sodium chloride solution, by means of a fixed volume micropipette. This was dried with an air blower, leaving a deposit of 8 μ g/cm² sodium chloride, which previous research has shown to be typical of 12 hours exposure in a marine atmosphere¹³.

The specimens were coated with vinyl acrylic (2:1) lacquer, the same lacquer as was used for previous experiments¹¹, four specimens (A-D) being made with adherent coatings and four (E-H) with non-

Figure 1
Specimen structure.

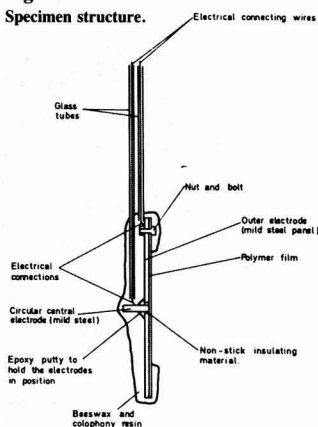
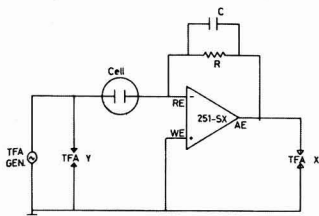


Figure 2
AC impedance circuit (two-electrode).



adherent coatings. The polytetrafluoroethylene/polyethersulphone was chosen as insulating material so that the lacquer would not adhere strongly to it, such that blistering would be able to occur unrestricted by this.

Electrical connecting wires were attached to each central and each outer electrode. The specimens were coated with beeswax and colophony resin such as to leave an unmasked area of 4 cm x 3 cm. A specimen is illustrated in Figure 1.

The specimens were immersed in aerated 3% sodium chloride solution (pH 6.30, conductivity 21 mS/cm). Measurements of galvanic current flow were taken on each specimen over a time period of 1100 hours, using the zero resistance ammeter used in previous work¹. The measuring system was arranged such that the two electrodes of each specimen were electrically connected to each other throughout the experiments, except when the connection was broken to take the current flow

readings.

AC impedance measurements were also carried out, using the centre and outside of each specimen as electrodes in a two-electrode system, as illustrated in Figure 2. The transfer function analyser was a Solartron 1174, the potentiostat used was an HB Thompson Ministat 251-SX, and the system was controlled by a Hewlett-Packard HP-85 computer, using a program entitled "IRNCAP", which was written by research workers in the Corrosion and Protection Centre, UMIST. The measuring resistor used was 10k ohm, and the measuring capacitor 33pF. The driving voltage was 10mV.

Experimental Results and Discussion

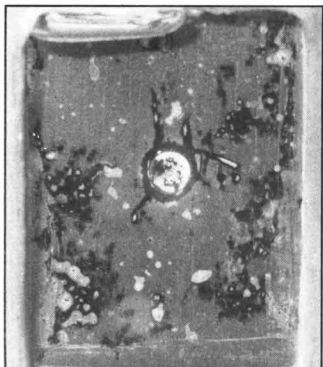
Corrosion was first observed within 30 hours of immersion, i.e. a blue colouration was first observed, which then turned black. This was located on the centre electrode, and was therefore presumably promoted by the sodium chloride contamination. The initial electron flow was from the centre to the outside on all the specimens, denoting anodic activity at the centre and cathodic activity adjacent to it. The currents involved were less than 100nA.

After about 100 to 200 hours, there was a tendency for blue, brown, and black patches to appear on the outside electrode, scattered around the centre electrode. These patches tended to be larger on the specimens with non-adherent lacquer films, and are illustrated in Figure 3 and 4.

Direction of current flow between the centre and outside electrodes tended to change frequently, and apparently randomly, on all specimens, although it could usually be correlated with observed colour changes. It should be noted that the appearance of a specimen with a dark area in the centre surrounded by a relatively less corroded region after a given time period did not show that the centre had supported anodic activity throughout that time

Figure 3

Specimen A after 411 hours in 3% sodium chloride solution, showing relatively large areas of corrosion on and around the centre electrode. (This specimen had a non-adherent coating.)



period, but only indicated that it had been a site of anodic activity during some of that time period.

The complexity of the corrosion reactions occurring can be appreciated by the fact that colour changes were observed from blue to black, blue to brown, brown to black, and black to brown.

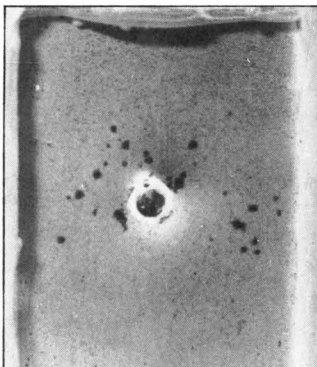
Eventual cracking of the coating was accompanied by relatively large current flows of several thousand nanoamperes and followed by widespread brown and black areas of corrosion, as may be seen from Figure 5. Cracking occurred first on the specimens with non-adherent lacquer films, after about 500 hours. After 1100 hours, only on one of the specimens with adherent films had the paint film cracked (after 700 hours). The onset of film breakdown did not appear to be related to the initial corrosion promoted by the contamination.

A.C. impedance measurements were carried out after 100, 250, 360 and 750 hours.

The impedance response normally obtained from a lacquer or paint-coated specimen has been attributed to the paint film acting as a resistor and capacitor in parallel, together with a component representing diffusion, and a component representing the resistance of the solution in which the specimen is immersed, according to the work of

Figure 4

Specimen E after 411 hours in 3% sodium chloride solution, showing relatively small areas of corrosion on and around the centre electrode. (This specimen had an adherent coating.)



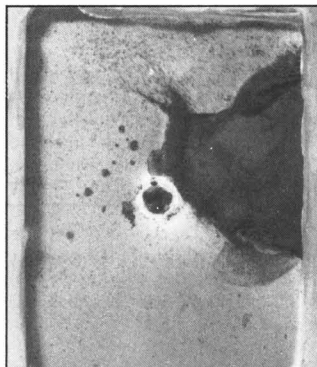
Piens and Verbist¹⁴, Scantlebury and Sussex¹⁵, and Callow and Scantlebury¹⁶, the commonly accepted equivalent circuit having been proposed by Piens and Verbist¹⁴. The contributions from the double layer capacitance and charge transfer resistance have been found to be negligible, and therefore not observed on the impedance plot, for a relatively intact coating^{14,16}. Piens and Verbist¹⁴ have associated the semi-circle of a typical response with the lacquer coating, Scantlebury and Sussex¹⁵ have related the high frequency intercept to the resistance of the electrolyte, and Callow and Scantlebury¹⁶ have ascribed the low frequency "tail" to diffusion controlled processes.

If the semi-circle on the Nyquist plots are taken as representing the response due to a resistor and capacitor in parallel, the values of the capacitance are given by the slopes of plots of angular frequency against the imaginary component of admittance. Similarly, the values of resistance are given by the slopes of plots of the product of the angular frequency and the imaginary impedance component against the real impedance component.

The value of capacitance obtained in our experiments were of the same order of magnitude as those obtained by Scantlebury and Sussex¹⁵ from chlorinated rubber coatings, and these capacitance

Figure 5

Specimen E after 850 hours, showing cracking of the coating and widespread corrosion.



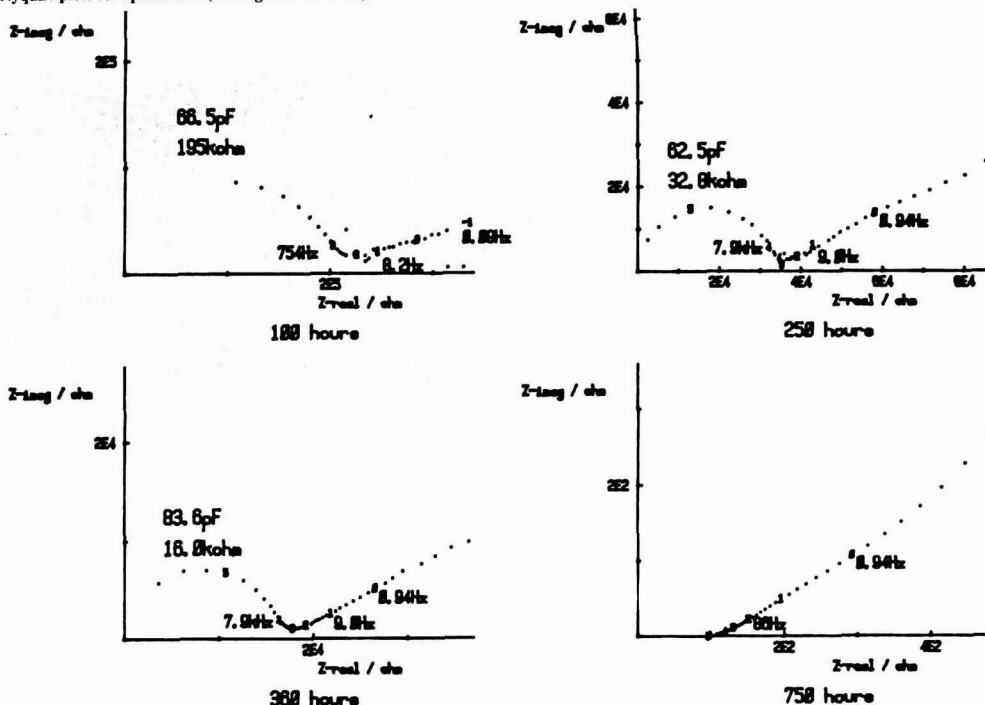
values may be reasonably attributed to the capacitances of the coatings, and hence the values of the resistance may be attributed to the resistance of the coatings.

Specimens A-D, i.e. those with a non-adherent coating, showed very similar behaviour to each other throughout the tests. They all initially gave a Nyquist plot showing a semi-circle and a diffusion tail, the semi-circle gradually decreasing in size until it disappeared altogether, this correlating with a significant increase in measured current flow, an increase in observable corrosion, and cracking of the lacquer film. The impedance responses are illustrated in Figure 6.

As corrosion currents were measured within a few hours of immersion, it seems that some water penetrated the lacquer to the metal surface soon after immersion, as also did some oxygen if the principle cathodic reaction was oxygen reduction, as suggested by many research workers, including Meyer and Schwenk¹⁷.

Increase in capacitance of coated metals before the onset of corrosion has been related to water uptake in the coating by Brasher and Kingsbury¹⁸. It is suggested that, as the capacitance values obtained for specimens A-D remained about the same order of magnitude between 100 and 360 hours after immersion, there was little water uptake after

Figure 6
Nyquist plots for specimen 8 (coating non-adherent).



the first 100 hours of immersion. The underfilm contamination appeared to promote a little corrosion, within the first 100 hours in particular, as judged by visual observations. However, the actual breakdown and cracking of the lacquer, accompanied by large increases in visible corrosion, plus the establishment of a totally diffusion controlled mechanism, appeared to be unrelated to the initial contamination, which is in agreement with our previous work¹.

Arrival of aggressive ions at the coating-metal interface has been linked with the onset of corrosion by Schober³ and Bellobono et al⁴ and it is thought that the penetration of ions into the coatings of specimens A-H was responsible for the gradual lowering of the resistances of the lacquer films, which is what the gradual decreases in radii of the semi-circles on the impedance plots are taken to represent.

The work of Schober³ and

Bellobono et al⁴ showed that a rapid increase in corrosion coincides with permeation of ions completely through a lacquer film. Once chloride ions had permeated completely through the lacquer films on specimens A-D, reaction between the iron of the substrate and the chloride ions could lead to the formation of a concentrated solution of iron chlorides at the substrate-coating interface. Osmotic pressure differences might then cause a sudden influx of water, which could well be responsible for causing the cracking of the lacquer film, due to mechanical stress imposed. Figure 7 illustrates this hypothesis.

The specimens with adherent lacquer films, i.e. E-H, showed rather different behaviour from specimens A-D, and no two of these were the same. At first sight, this seems surprising, but not if considered in the light of the inhomogeneous nature of polymer coatings, as demonstrated by Mayne and co-workers^{19,22}.

Specimen E exhibited a diffusion-controlled mechanism throughout. It is suggested that there were probably large pores through the lacquer coating, through which ions were able to diffuse at all times. However, the adhesion of the coating to the substrate would retard or prevent diffusion of ions along the metal/coating interface. Presumably water would also find difficulty in diffusing along the metal/coating interface if there were good adhesion between the metal and coating, and it is suggested that a water layer is not formed so easily between the metal and coating as in the specimens with non-adherent coatings.

Specimen E showed a decreasing solution resistance with time on the AC impedance diagrams, and it is suggested that ionic diffusion became possible through a greater number of pores as time of immersion increased, due to increased uptake of ions into the film. However, the only conducting pathway between the centre and

Figure 7

Hypothesis for the corrosion mechanism on the specimens with non-adherent coatings.

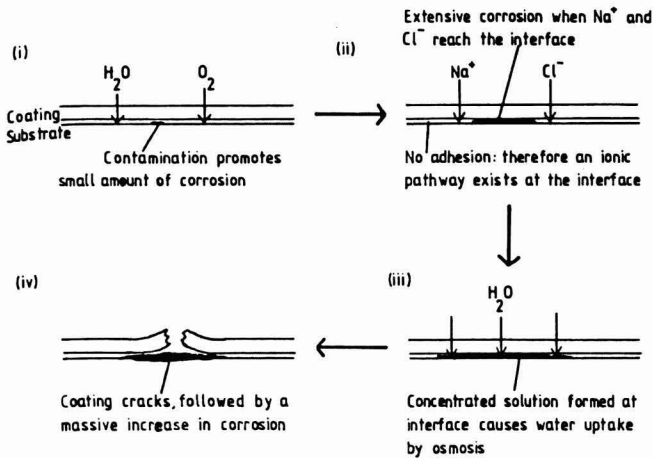
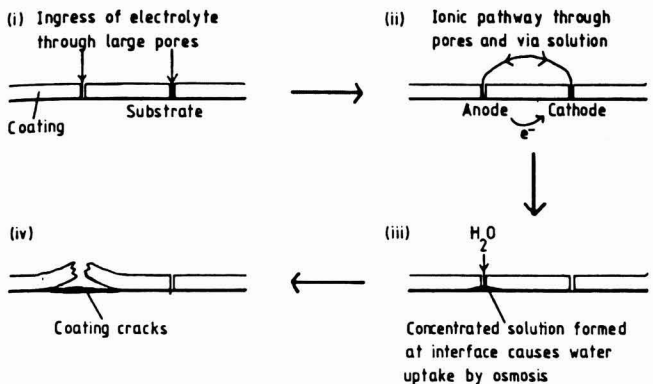


Figure 8

Hypothesis for the corrosion mechanism on specimen E (coating adherent), which gave a diffusion-controlled Nyquist plot throughout.



outside electrodes appears to have been via the coating and the solution. Eventually, the combination of ion permeation through the coating, water forcing its way slowly along the metal/coating interface, localised formation of small regions of concentrated iron chloride solutions, and osmotic permeation of water thus promoted are thought to have cracked the coating and allowed free flow of electrolyte underneath the coating, giving widespread corrosion. The proposed behaviour is illustrated in Figure 8.

Specimen G showed a semi-circle on the impedance plot for the first

250 hours, but thereafter resembled specimen E.

Specimen F somewhat surprisingly showed an increase in the size of the semi-circle on the impedance plot between 100 and 250 hours. Possibly this was due to the pathway between the centre and outside electrodes being through only a few isolated pores. If these became blocked at the base with corrosion products, then an increase in lacquer film resistance might occur, giving a larger semi-circle on the impedance plot. In support of this, there were noticeably fewer corrosion spots on the outside electrode than on specimens E and G, suggesting the

presence of fewer pores. The size of the semi-circle decreased later, and total diffusion control had been established after 1200 hours. Figure 9 illustrates this.

Specimen H was a special case, because in making the substrate, it was found that a hole was left in the insulation material in the gap between the centre and outside electrodes. After several attempts to fill in this hole with polytetrafluoroethylene/polyethersulphone had failed, it was decided to coat the specimen as it was with a lacquer film, and proceed with the experimentation on it.

Specimen H showed a diffusion-controlled impedance response throughout immersion, accompanied by the flow of relatively large currents of at least several hundred nanoamperes, and sometimes several thousand nanoamperes. This specimen was particularly interesting because a blister grew over the hole in the insulation, thereby covering small areas of both the centre and outside electrodes, as well as the gap between them, as shown in Figure 10. The colour of the blister was a light brown, with the part on the centre electrode being dark brown. Electron flow was from the outside electrode to the centre, suggesting that the anodic reaction was principally located on the outside and was presumably the oxidation of iron to iron (III).

The cathodic reaction, located on the centre, was probably principally oxygen reduction, as proposed for example by Meyer and Schwenk¹⁷. The alternative cathodic reaction proposed by Gonzalez et al²³ and Kotova and Kanevskaya²⁴ of the reduction of iron (III) to triferric tetroxide was probably responsible for the appearance of the dark brown coloration on the centre electrode.

Changes in the electron flow direction occurred after about 600 hours and back again after 800 hours. The whole blister had become a darker brown after 1100 hours, with a few spots of black.

Figure 9
Nyquist plots for specimen F (coating adherent).

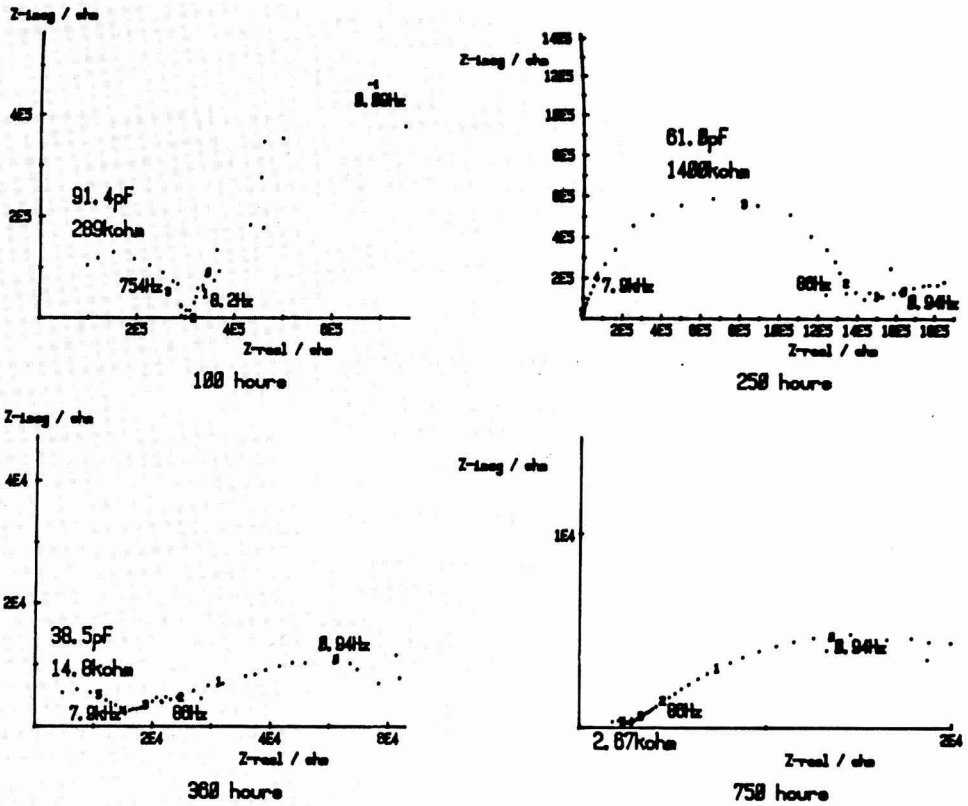
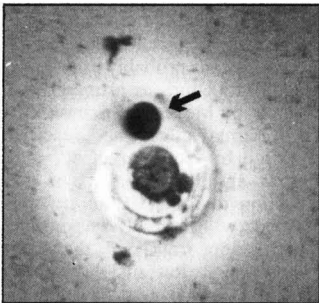


Figure 10
Specimen H after 411 hours in 3% sodium chloride solution, showing a blister having grown across the gap between the centre and outside electrodes.



Probably a large physical defect existed in the lacquer film where it had been applied across the hole in the insulating material. Electrolyte solution would be able to flow freely into the hole, giving a free

corrosion situation. Dissolution of iron would give a concentrated solution, causing influx of water, due to osmosis, and the growth of a blister, as illustrated in Figure 11.

An additional experiment was performed in which specimen H was removed from the tank of aerated 3% sodium chloride and placed in another vessel of 3% sodium chloride solution (after 1200 hours). This was then deaerated by bubbling nitrogen through for 30 hours. The impedance plots before and after this operation were almost identical, as can be seen in Figure 12, both plots showing a diffusion controlled mechanism. A blackening of the brown corrosion product was observed, suggesting the reduction of iron (III) oxide to ferric tetroxide as a cathodic reaction occurred faster when oxygen was absent, as would be

expected, as the reduction of oxygen would be unable to occur as a cathodic process.

The almost identical impedance plots before and after deaeration showed that the diffusion control was not related to the diffusion of oxygen through the lacquer, and therefore the diffusion control must presumably have been related to ionic diffusion.

Conclusions

1. The most important factor determining the degree of protection of the metal substrates by the polymer coatings is the physical structure of the coating, and particularly any defects in the coating.
2. Corrosion is thought to be promoted by chloride ions being

Figure 11

Hypothesis for the corrosion mechanism on specimen H (coating adherent).

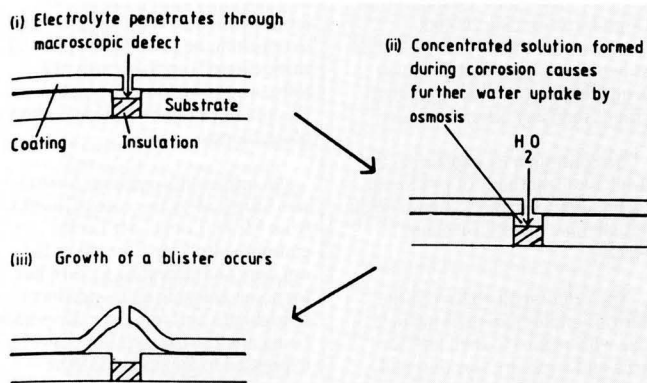
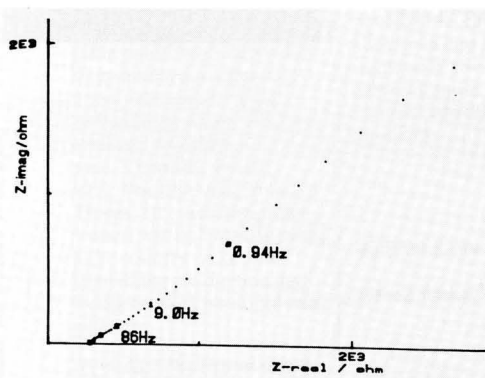
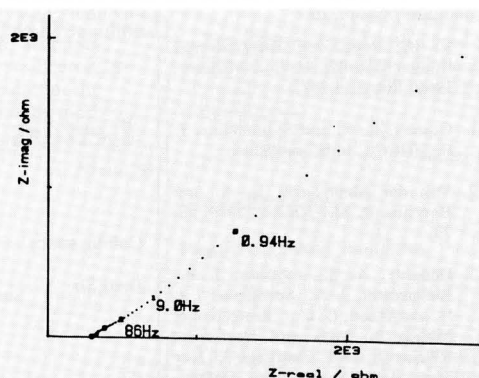


Figure 12

(a) Nyquist plot for specimen H after 1203 hours immersion in 3% sodium chloride solution (aerated).



(b) Nyquist plot for specimen H after 1234 hours. (Transferred to deaerated 3% sodium chloride solution after 1205 hours.



able to diffuse through any physical defects in the coating to the coating-substrate interface.

3. The beneficial role of adhesion is in impairing the formation of a layer of electrolyte at the coating-substrate interface, and thus in preventing the spread of the macroscopic areas of corrosion over the substrate surface.

It is proposed that this electrolyte layer at the interface would consist of a relatively concentrated solution with respect to the external solution, and could thus promote further uptake of water through the coating due to osmosis, and that this might cause cracking of the coating.

4. Although the initial contamination underneath the coating may have promoted a little corrosion initially, the time before the onset of a significant degree of corrosion accompanied by coating breakdown was of comparable duration for contaminated and uncontaminated specimens, and the presence of contamination at the level used in our experiments ($8\mu\text{g NaCl}/\text{cm}^2$) is not thought to have been a major factor.

5. The corrosion processes within a blister are governed by a diffusion controlled mechanism. This is related to the diffusion of ionic species, and not to the diffusion of oxygen.

Acknowledgements

We wish to thank Professor G. C. Wood for provision of laboratory facilities and also the Science and Engineering Research Council Marine Technology Directorate for providing a research studentship.

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London Section

Carbon black pigments

For those members who have ever experienced problems with carbon black pigments in the past, you may have missed an excellent opportunity to improve your knowledge of this important pigment group.

The fifth technical meeting entitled "Carbon blacks from production to application in coatings" was presented at The Naval Club by Mr A. Elbrechter of Degussa AG Germany on Wednesday 17th February.

Continued from p.120

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Mr Elbrechter identified the world usage of carbon black as some 4 million tons annually with Degussa producing 200,000 tons/year. Of this 10% is produced as pigment grades with Degussa producing more of these pigment grades than any other producer.

He continued by explaining the three basic methods of producing carbon blacks namely: Lamp black, gas/channel blacks, furnace blacks.

The relationship between the various grades and their particle size with regard to their surface area and structure was outlined, together with the advantages and disadvantages of the various processes and grades. The form in which the grades are available i.e. powder vs beaded blacks was highlighted together with their tinting strengths.

The oxidation process used on certain grades to improve the dispersability and to modify the jetness/blueness was explained and to conclude he presented a piece of work carried out to identify the influence of various parameters on the hue of titanium dioxide/carbon black blends.

An interesting question session was followed by the vote of thanks from Mr N. Locke. Mr Locke complimented Mr Elbrechter for not only an interesting lecture but for some amusing slides produced to highlight and reinforce the points being made. Appreciation was also expressed to Degussa for their sponsorship of the evening.

P. C. Neal ■

Continued overleaf

Letters

Colour space

Dear Sir,

In his description of the value of colorimetry in the field of printing inks¹ Nobbs mentions that one defect of CIELAB colour space is that the psychological primaries do not lie on the a*b* axes "as originally intended". This was not, however, the original intention because if this occurred the resulting colour space would not be uniform with respect to hue. At the same lightness and chroma, psychological primary red is perceptually nearer to yellow than to blue by a factor² of at least 2:1. As uniformity was the only objective in the case of CIELAB and its 1944 precursor, ANLAB, this lack of orthogonality was considered to be unimportant. The Swedish Natural Colour System, on the other hand, is based on orthogonality but cannot be used for quantifying colour differences.

7 Bucklebury Place
Upper Woolhampton
Berks RG7 5UD

Yours faithfully,

K. McLaren

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1. J. H. Nobbs, *JOCCA*, 1986, 297.
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Manchester Section

Works visit to BASF Graphics,
Cheadle Hulme

On Monday 15 February 1988 a party of 37 members and guests were able to visit the Graphic Arts Division of BASF at Cheadle Hulme.

After an initial reception when coffee and biscuits were served the party were introduced to the BASF Staff – John Wilson, Jim Barrie, David Thorpe and Alan Garnett – before being split into three groups.

By alternating the groups we were able to see:

1. A corporate video of BASF showing the much wider fields the company is involved in other than cassette and video tapes. These fields are Pigments, Dyes, Plastics, Agrochemicals, Flavours, Fragrances, Vitamins, Resins, Computers, Printing Inks, Printing Plates, Drugs, etc, indicating that their products will be found in every home in the country. A second video detailed the production and use of Nyloprint/Flex photopolymer printing plates.

2. Preparation of Nyloprint plates. A demonstration was given by John Wilson in the showroom of the water wash process of making plates for Letterpress printing. After exposing the plate through a negative using UV light for 2 minutes, automatic washing for 5 minutes with water, then drying ensured that a perfect plate was produced for the commercial printer. Nylolith for litho printing and plates for newspaper printing that can be prepared in under 5 minutes were also discussed.

3. A further demonstration for the preparation of Nyloflex plates used in Flexographic printing was given by Alan Garnett. Exposure here was much longer at 10 minutes, washout of the unreacted photopolymer was with a mixture of perchlorethylene and n butanol in a three stage process before drying

for a minimum of 2 hours and then undertaking a finishing process. Effects of under and over exposure were demonstrated.

It is also possible to produce gravure plates in a similar process at much lower costs than conventional cylinders, however a technique of joining the plates round a cylinder without a mark for continuous designs has not yet been overcome.

Over all the different types of plate BASF supply, 79 variations exist with varying backing material, thickness, depth of relief, etc.

Following this excellent, lucid explanation and demonstration a sumptuous buffet with wine was served.

The normal vote of thanks was not feasible, therefore the Chairman and Hon. Secretary thanked BASF most sincerely on behalf of those present for the courtesy offered and the food provided.

M. Nixon ■

Midland Section

Aerosil fumed silicas

A technical meeting of the Midland Section was held on the 18 February 1988 at the Clarendon Suite, Stirling Road, Edgbaston, Birmingham. Members and guests heard Mr A. Elbrechter of Degussa Ltd give a talk on "Aerosil fumed Silicas for the Paint Industry".

The speaker started his talk by outlining the history and production of fumed Silica. The first patent for Pyrogenic Silica was taken out in 1941 and commercial production started in 1942. These ultra fine silicas have a primary particle size of between 7-10 nanometres and a surface area of 90-380 M²/g. They were originally used as reinforcing agents for rubber but today they have many uses, such as thickening and structuring agents for paints and free flow agents for powders.

The Aerosil particles contain Siloxane and Silanol groups and it is the Silanol groups that impart hydrophilic properties to the Silica. These groups can be chemically modified to produce hydrophobic types.

Thorough dispersion of the Aerosil is necessary to achieve the desired properties and high speed stirring is usually not sufficient. The most effective way is to use the Master Batch technique. Here, depending on the dispersion equipment used, concentrated bases containing 3-12% Aerosil can be produced.

Throughout the talk Mr Elbrechter showed numerous slides to illustrate the various types and uses of Aerosil with typical results that can be obtained.

The meeting closed with a vote of thanks proposed by Mr E. Wallace and endorsed by the audience in the usual manner.

B. E. Myatt ■

Newcastle Section

Pressure sensitive laminates

The fifth meeting of the 1987/88 session was held on 4 February 1988 at St Mary's College, University of Durham, when twenty-six members attended to hear local member Mr Neil Redpath of Fasson Adhesives give a lecture on "Pressure-Sensitive Laminates – Making Sticky Labels".

Mr Redpath gave a brief history of labelling, from the Egyptians (100BC) to the first commercial use by Guinness, of printed paper labels (using animal glue); the modern adhesive era introduced by 3M's Cellotape, and the first paper-backed tape in 1935. The latest pressure-sensitive laminate design was the culmination of much development, which is continuing and typically consists of five parts; a facing paper, primer, adhesive, silicone release treatment and backing paper.

Occa meetings

Face papers can be thin (15µm), thick (200µm), plastic, coloured, fluorescent, even thermally sensitive for heat marking. Priming is necessary to prevent adhesive migration into the paper, which reduces paper strength and causes discolouration. Adhesives used are often rubber-based, sometimes emulsified, solvent thinned or hot-melt: viscosities, solids and application thicknesses vary considerably. Silicone release materials are usually applied from very dilute solution but solvent-free forms are also used. Backing papers need to have good hold-out for the silicone treatment whilst providing some key for silicone at the same time.

Mr Redpath gave an interesting account of the massive machinery used in manufacture, with excellent coloured slides and samples of a number of different types of label, as supplied in strip form, including one for an expensive brand of Scotch whisky. Each stage of the process was discussed, with a few examples of potential defects in the finished product and how these are avoided. Quality control involves a number of tensile and shear adhesion tests, as one would expect, and a staining technique for checking uniformity and thickness of the release coating.

The interest aroused in the talk was demonstrated by the intense questioning and discussion which ensued. Topics ranged from a major application for aircraft permanent markings, removable versus permanent labels, peelable-backed postage stamps and why so many supermarket items have labels which are admittedly difficult to remove.

The Chairman, Mr S. Lynn, gave the vote of thanks, after which the usual first class buffet meal was enjoyed by all.

J. Bravey ■

OCCA ties at £4.25 each are available from the Association's offices, with a single Association Insignia on either a blue or maroon background.

South African Division Transvaal Section

Decorative paints

A discussion meeting was held by the Transvaal Section on the 17 February 1988 entitled "Decorative paints used on buildings".

In the discussion team were: Mr T. Edwards, Chairman; Mr A. Staub representing the building industry; Mr P. de Villiers representing the painting contractors and Mr G. Harmsworth representing the paint industry.

The discussion started with Mr Staub and the main points he put forward were:

1. In the home building industry the final finish is most important but cost is also a major factor.
2. Because of the competition when quoting it was necessary to specify a standard which was readily available on the market to contractors and they requested a South African Bureau of Standards approved product or an equivalent quality. Inferior paints were still however being used.
3. He felt that the paint industry did not promote the new products to the building industry and this should be done so that they become more aware of new products.
4. The quality of our painters are poor and the industry is depleted of good artisans. More training should be made available to train painters.

Mr de Villiers speaking from the subcontracting aspect put forward the following points:

1. On large projects he often encountered specifications which were too broad and often led to smaller contractors under-specifying in order to get the contract.
2. Because one needs very little capital to start up as a painting

contractor there were too many "Have brush will travel" painting contractors around.

3. The main contractor always has a problem with time and the painting contractor is one of the last on site and they usually have to make good, final patching up done by the electricians and plumbers etc.

4. Technical support from the paint industry was generally good but a major problem was receiving supplies on time, specially when fancy colours were required. Another major problem was colour difference with different batches of the same colour. This resulted in extra costs as you could not touch up small areas.

Mr Harmsworth speaking from the paint manufactures' point of view made the following points:

1. Most complaints come through contractors trying to take short cuts like applying one coat when two coats are required. This often comes about due to wrong estimating or the painters stealing and then adulterating the rest to try and make it go further.
2. When investigating complaints you often come across people who are unqualified but think they know all the answers and will not accept the findings of a qualified paint chemist. He called these people "bush chemists".
3. On major building projects more use should be made of paint companies or appropriate bodies to ensure that the painting specification is satisfactory.

The meeting was attended by an enthusiastic audience and a lively question time followed. The vote of thanks was given by Ted Wright.

L. Saunders ■

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Scottish Section Annual Dinner Dance

The Annual Dinner Dance of the Scottish Section was held on 15 January at the Hospitality Inn, Glasgow. There was an excellent turnout of 300 members and guests including principal guests the OCCA President and Section Chairmen from Manchester and Thames Valley Sections with their wives. Once again an excellent meal was provided with haggis as a starter course. Hugh Munro, Scottish Section, performed the address to the haggis. The main course of Roast Barron of Beef was ceremoniously carried into the room led by a piper. The OCCA President Mr J. Bourne carved the first slice. Following the meal Simon Lawrence, Chairman Scottish Section, toasted the health of the guests. Mr Bourne replied on behalf of the guests. A lively evening's dancing followed the meal with entertainment provided by the 'Receivers'.

R. A. Hunter ■

OBITUARY

Richard Cecil Somerville

Mr R. H. Hamblin writes:

With the death of Dick Somerville in February, just days before his seventy-ninth birthday, both the Association and the Irish Section have lost a good friend and supporter.

In addition to serving on the Section Committee, he held office at various times as its Hon. Secretary, Hon. Programmes Officer and Hon. Publications Secretary. He twice represented the Section on Council, being nominated by Council as a Vice President (1978-80) during his second term of service.

Assiduous in his attendance at Council Meetings, he reported fully

1988(4)



Scottish Section Dinner Dance guests (L to R): Fred (Chairman, Manchester Section) and Vera Morpeth, John (Chairman, Thames Valley Section) and Hilary Inshaw, John (President) and Hilary Bourne, Raymond (Vice Chairman, Scottish Section) and Isobel Hill, Simon (Chairman, Scottish Section) and Jane Lawrence.

on the Section's activities and constantly sought to further its development. His quiet, unassuming manner endeared him to many members of Council and to the headquarters staff. He had a life-long connection with Bergers and was pleased to see the formation of an Irish Branch of the Bristol Section, which later became the Irish Section of the Association.

Retaining his interest in the Section in retirement, he was always willing to assist in publication matters, being the Section's Hon. Publications Secretary until 1987.

To his widow and son the Association extends its deepest condolences. ■

New members

The sections to which new members are attached are shown in italics together with the country, where applicable.

Ordinary members

Ball, M. J., PhD (*Transvaal*)

Bing, S. I. (*Transvaal*)

Chadha, C. S., MSc (*General Overseas - India*)

Grady, D. T. (*Transvaal*)

Marche, J. P. (*Transvaal*)

Martin, P. J. (*Irish*)

Meyer, C. R. BSc (*Newcastle*)

Nicholson, P. (*West Riding*)

O'Donovan, P. G. (*Transvaal*)

Patel, B. (*General Overseas - India*)

Rutherford, D. J. (*Newcastle*)

Simpson, A. G., MSc (*West Riding*)

Tannock, J., BSc, PhD (*Zimbabwe*)

Villa, G., BSc (*General Overseas - Italy*)

Woodhouse, A. D., BSc (*Newcastle*)

Associate members

Berry, A. C. (*Manchester*)

Frijns, C. E. (*Transvaal*)

Kirten, H. A. (*Transvaal*)

McMillan, N. (*Transvaal*)

Rich, J. (*Transvaal*)

Teare, G. K. (*Manchester*) ■

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**Mrs. A. Lye,
Buckman Laboratories Ltd.,
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Lloyd Street North, Manchester M15 4EN.**



Buckman Laboratories Limited

SITUATIONS VACANT

As the Major UK Selection Consultancy which specialises in Appointments for the Surface Coatings Industries we are retained to advise on the following jobs:



1. **Screen Inks Graduate** (30-35), with at least seven year's experience, to work with owner of 2 million dollar growth company in New Jersey, to diversify existing products from textile plastisol inks and screen chemicals, to plastisol puff inks, water based textile inks, polyethylene bottle inks, thermal cure inks and UV. This is a truly exceptional opportunity to gain top appointment through development, trial and service in well resourced New Jersey company. AMERICA Initial salary **35,000 Dollars p.a.**
2. **Liquid Inks Product Manager**, (30-35), to be responsible for advanced product presentation trial, and top level service to major flexible packaging accounts. SOUTH WEST **£20,000 p.a. + car**
3. **Graduate Oil Inks Chemist**, (30-40) for R&D, product development, senior servicing and factory and brand management appointments (5) for substantial and very successful East Coast independent organisation with two base factories and eight branches. AMERICA Salaries to **45,000 Dollars**
4. **Graduate or PhD Ink or Paint Chemist** to be appointed as technical manager for specialised inks, development advanced formulation, service and quality through staff of 20, for major international company. Specific experience of inks not essential. The company is particularly interested in experience of innovative resins development and "polymer engineering". AMERICA **60,000 Dollars p.a. + car**
5. **Works Manager**, (c40) for major UK and international coatings company. The job involves total control of manufacture from materials supply to distribution, together with services for important group factory. SOUTH **£20,000 p.a. + car**
6. **Chief Oil Inks Chemist**, (graduate 30-40), for an established profitable growth company, well respected throughout the industry. Responsibility is for development, customer services, and top level customer liaison with the independent opportunity to develop new technology for a comprehensive range of oil inks. Prospects are exceptional. SOUTH **£20,000 p.a. + car**
7. **Oil Inks Product Development and Service Manager** for a medium sized but growing organisation. Responsibility includes short term and customer development, advanced formulation and quality together with service. SOUTH EAST **£15,000 + and car**
8. **Master Batch Technologist** for product development and technical service for colourants for plastics marketed, throughout the UK, by well established leading company with strong technical backing and R&D resource. SOUTH **£14,000 + car**
9. **Newly Qualified PhD Chemist** to join R&D laboratories of strong adhesives organisation. To contribute, after formalised training to innovative technology backed by exceptional resource in modern laboratories. SOUTH **£14,000 p.a.**
10. **Graduate Chemist** for major company as account executive for ranges of surfactants marketed to textile, paper and coatings industries. Sales or product presentation experience essential. NORTH **£17,500 p.a. + car**
11. **Senior Protective Coatings Sales Executive** (30-40), for major UK organisation. Experience of specification selling and presentation to engineering consultants, architects and major structural steel and building contractors essential for the progressive sales and marketing appointment. LONDON **To £20,000 + car**
12. **Colourist** (25-30), for coatings for plastic to be responsible for colour standards to meet particularly automotive and component specifications for most major UK manufacturers together with colour specification for radio, TV and audio industries. SOUTH EAST **To £14,000 p.a.**

Candidates for these appointments or for others on our expanding list of career jobs are invited to write in confidence to:

G. P. Birtles. SITA Selection, 203 Gardiner House, Broomhill Road, London SW18 4JQ or to telephone 01-871-5011/2.

We maintain a register of over 1600 persons with experience of Surface Coatings. We will be glad to include your name on it and then keep in touch with suitable advancement opportunities as they become available through us. **LUCENE SE6026**

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OIL & COLOUR CHEMISTS' ASSOCIATION

SURFEX

88

Exhibition of the latest developments in raw materials and equipment used in the manufacture of paints, printing inks, colour, adhesives, sealants and allied products to be held at the

HARROGATE INTERNATIONAL EXHIBITION CENTRE YORKSHIRE, ENGLAND

Wednesday, 15th June, 1988
09.00 - 17.30 hours

Thursday, 16th June, 1988
09.00 - 17.30 hours

ADMISSION FREE

The "Official Guide" will be circulated in the May 1988 issue of the Association's Journal (JOCCA) and will also be freely available at the entrance to the Exhibition. Advertising space for the Official Guide can now be booked by contacting
Frank Craik on 01-908 1086.

ACCOMMODATION SERVICE

To assist in arranging accommodation in Harrogate, contact
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AIR TRAVEL

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Leeds Airport on (0532) 509696.

SYMPOSIUM

As an associated event the Paint Research Association will be holding a symposium on "Towards better Industrial Finishing" on 13-14 June, 1988, Cairn Hotel, Harrogate.

For further information contact
Dip Dasgupta at PRA on 01-977 4427,
Telex 928720

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