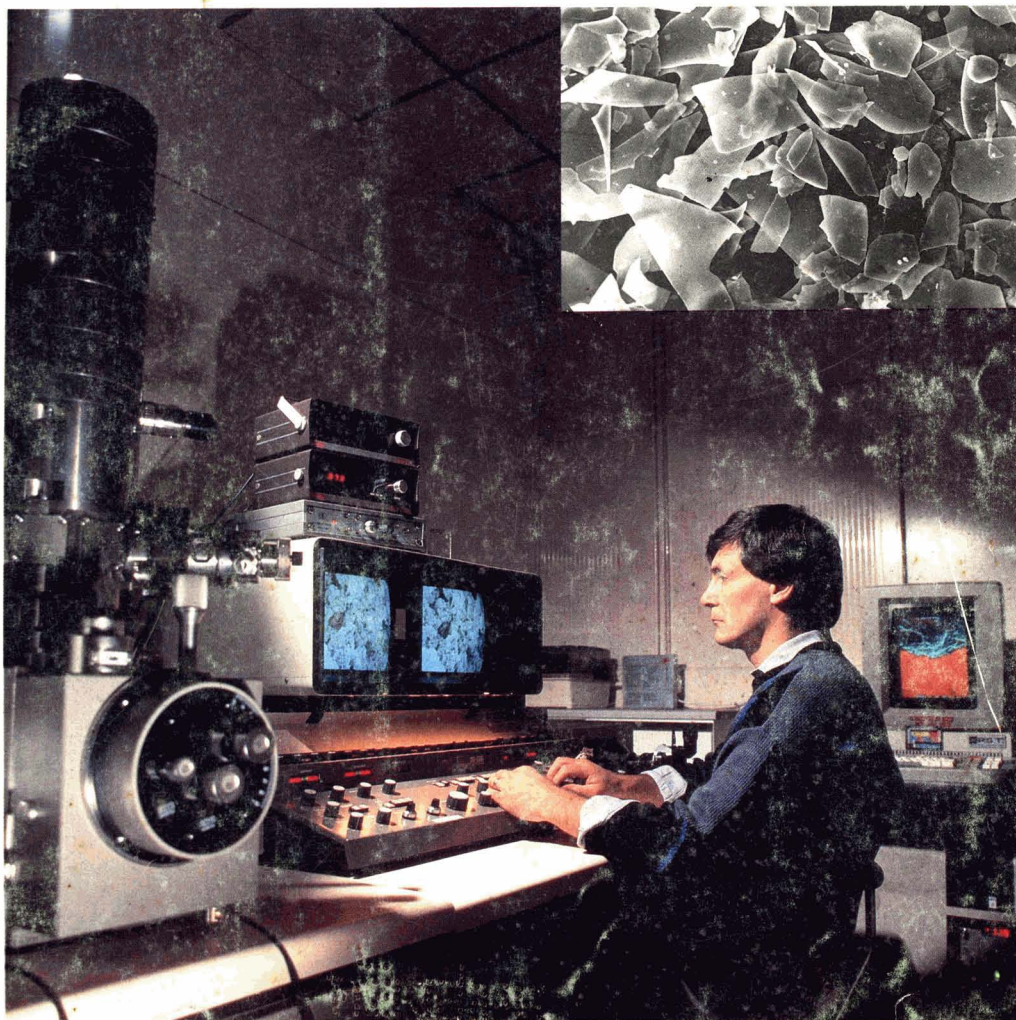




JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION

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Member of the
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An official Journal of the
Paintmakers Association
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Contents

News	2
Feature: Corrosion	
Synthetic micaceous iron oxide: A new anticorrosive pigment by E. V. Carter and R. D. Laundon	7
The rate of hydration of zinc phosphate incorporated in a paint film by P. J. Gardner, I. W. McAra, V. Barton and G. M. Seydt	16
Evaluation of anticorrosive paint binders by means of AC techniques: Influence of chemical composition by A. R. Di Sarli, E. E. Schwiderke and J. J. Podestá	18
Underfilm corrosion of steel induced by saline contaminants at the metal/paint interface by M. Morcillo, L. S. Hernández, J. Simancas, S. Feliu Jr. and S. Giménez	24
Transactions and Communications	
Tainting — an analyst's approach by D. L. Easterby	29
Process Operation	
Dispersing and Mixing	31
Standards Focus	34
Horizons	
Activities of the European Federation of Corrosion	35
Conference Monitor	
UK Corrosion '89	36
Organotin Antifouling Compositions	39
Book Reviews	40
From the General Secretary	41
OCCA Meetings	43
OCCA News	46

Cover: Examination of the new anticorrosive pigment, Synthetic MIO (top RH corner) by scanning electron microscopy — see p.7 (Photo by courtesy of Cookson Group, Central Research).

Forthcoming Features: February — Quality Assurance; Process Operation (PO), Computer Controls, March — Adhesion; PO, Filtration, April — Polymers and Resins; PO, Metering Equipment.

Contributions are welcomed at least five weeks prior to publication date.

JOCCA (ISSN 0030-1337) is published monthly by the **Oil and Colour Chemists' Association**, Priory House, 967 Harrow Road, Wembley HA0 2SF, England Tel: 01-908 1086 Fax: 01-908 1219 Telex: 922670 (OCCA G)

1990 annual subscription rate: UK £82.00, rest of the world (excluding USA) £90.00, USA \$180.00. Single copies £8 (\$16).

Air freight and mailing in the USA by Mercury Airfreight International Ltd Inc., 2323 Randolph Avenue, Avenel, NJ 07001. Second class postage paid at Rahway NJ. US Postmaster send address changes to JOCCA c/o Mercury Airfreight International Ltd Inc., 2323 Randolph Avenue, Avenel, NJ 07001.

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

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

Ernstrom Group acquires Norwegian Talc

The Ernstrom Group of Gothenburg, Sweden has acquired Norwegian Talc (UK) Ltd, Nortalc Milling Ltd and the mineral processing and sales activities of Norwegian Talc throughout Europe. These companies will become part of Ernstrom Minerals. Ernstrom Minerals AB own huge mineral resources together with comprehensive production facilities for dolomite and feldspar situated close to Orebro.

Ink prices due to rise

Price rises across a broad range of printing inks and sundry items are forecast by the Society of British Printing Ink Manufacturers. These increases have been brought about due to the effects of higher costs for pigments, resins and other raw materials, including linseed and other vegetable oils, and of tighter allocations on certain materials such as titanium dioxide.

Alplas opens new offices and laboratory

Alplas Technology offices and laboratory were recently 'officially opened' by Mr W. W. Lane, President of Atlas Electric Devices with Mr S. Lane, President of South Florida Test Services and Mr R. Voelman, Managing Director of Atlas SFTS BV, Holland. The new offices are at Ferry Hinksey Road, Oxford with the testing laboratory operating on the same principles as those at South Florida Test Services (SFTS) and Atlas SFTS BV in Holland.

New Euro-consultancy

UK based Dick Mann Associates, International Industrial Marketing Consultants, and Miles Associates, Industrial Development Consultants, have this month announced a new consultancy service for smaller and medium sized European and US companies in the chemical and allied sectors of industry who are seeking to establish cross-border or inward investment projects within the European Community.



The CRAYNOR team (L to R): Jules Lefebvre, Robert Zwanenburg, Kevin O'Hara, Gerard Mongin, Annie Bernabe and Charles Hazan.

CRAYNOR – a new radiation curing company

The Coates/Orkem Group has formed CRAYNOR to supply products to the growing radiation curing market. Many of these applications are of strategic importance to the Coates Lorilleux, Coates Special Products, Coates Electrographics and Coates Coatings Businesses.

Recognising the specialist nature of the radiation curing market, Cray Valley Products and Norsolor decided to form a joint venture company, called CRAYNOR which would manufacture and supply the basic radiation curable chemicals—namely oligomers and monomers. Craynor's facilities comprise: Headquarters located at Puteaux on the outskirts of Paris, Plant at Villers St Paul (65 km north of Paris) and a Technical Service Laboratory located at Norsolor Research Centre at Verneuilen Halatte (60 km north of Paris).

Craynor's management team includes: Charles Hazan, Director General of Craynor and Cray Valley France. Mr Hazan, a graduate of UMIST in the UK, came from Norsolor and has extensive experience in the European Chemical Industry. Gerard Mongin, Commercial Director also from Norsolor has wide experience of sales and marketing in the chemical and plastics industry. Kevin O'Hara,

Technical Director who came from Cray Valley Products in the UK, has spent all of his professional life in the coatings industry and has been involved in radiation curing since its embryonic days 20 years ago. Rob Zwanenburg, Technical Manager who transferred to Craynor from Sartomer when its European operations in Holland closed down. Mr Zwanenburg also has a number of years' experience in the coatings industry having worked at Sigma Coatings in Holland before he joined Sartomer.

ICI Resins wins environmental award

ICI Resins b.v. in Waalwijk, the Netherlands, has been granted the 1989 Dutch Environmental Award for Industry, in the category "Environmentally Friendly Products". This category recognises preventive thinking in the early phase of product development, enabling the introduction of environmentally safe consumer products. The award relates to ICI's product grades NeoCryl acrylic dispersions and NeoRez polyurethane dispersions, both waterborne products which are used as raw materials in paints, inks and adhesives. Product development started in the early seventies when the first emission-related smog problems arose.

Titanium dioxide waste acid recycling plant starts-up

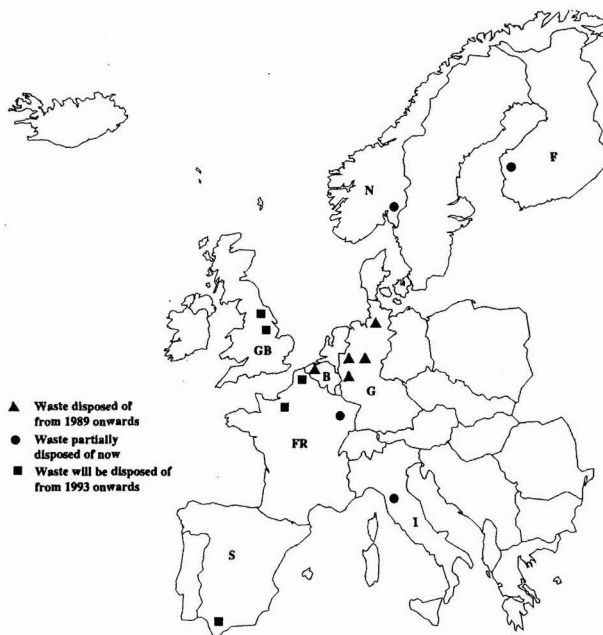
On 9 November 1989 the TiO_2 waste acid recycling plant (see July 1986 JOCCA, p195) was officially started-up at Sachtleben, Duisberg, W. Germany. In attendance was Dr G. Karus, Board of Directors, Metallgesellschaft AG; Mr H. von Kleist-Retzow, Chairman of the Board of Directors, Sachtleben Chemie GmbH; Prof Dr E. Ulrich von Weizsäcker, Director of the Centre for European Environment Policy, Bonn and a group of federal ministers.



The recycling plant has been constructed in just 2½ years at an investment of DM200 million to provide environmentally responsible TiO_2 disposal and recycling facilities for two German plants: Sachtleben Chemie GmbH, Duisburg, a member company of the Metallgesellschaft AG group, and Kronos Titan, of Leverkusen. These two titanium dioxide producers have resolved, in a cooperation agreement, on a joint waste product disposal concept, the centre-piece of which is formed by the waste acid recycling plant with its annual processing capacity of some 800,000 t waste acid. The Duisberg plant will enable Sachtleben to increase TiO_2 supply up to 85,000 t/year (+35%).

New HMG wood lacquer plant

H Marcel Guest has opened a new purpose-built lacquer production plant. This additional facility represents a £¼m investment for the group and a 30% increase in capacity, at its Manchester site. The new building incorporates advanced blending and dispersion equipment, designed to HMG's own specification, which will enable the efficient processing of different colour batches.



Titanium dioxide sulphate plants—location and waste disposal situation in Western Europe.

Synthite gains BS 5750

Synthite, the largest UK manufacturer and supplier of formaldehyde products, has achieved registration to BS 5750. The registration applies in respect of all formaldehyde, paraformaldehyde and Alcoforms products, and covers the company's operations at its sites in West Bromwich and Mold in North Wales.



Synthite BS 5750 presentation, Left to Right: Works General Manager, Dennis Chancellor; Director, Edward Thurgur; Laboratory Manager, Donna Mason; Director of Employment Affairs, Chemical Industries Association, Kenneth Hack; Managing Director, Harry Sharp; Chairman, Synthite and The Tennant Group, Kenneth Alexander; Engineering & Production Manager, Mold, Kevin Jones; Works Manager, Murray Preece.

OCCA South Africa Symposium: Call for Papers

OCCA South Africa will be holding its 13th National Symposium on 13-16 October 1990 at the Lord Charles Hotel, Somerset West on "3rd and 1st World — Coatings Towards 2000". The symposium will be organised by the Cape Section of OCCA. Social events will include a gala banquet, cocktail party and golf tournament. Authors wishing to present a paper should forward a 300 word synopsis by 31 January 1990 to John Copeland, The Organising Committee Chairman, 13th National OCCA Symposium, PO Box 428, Paarden Eiland, Cape 7420, South Africa. Tel: (021) 5112647, Fax: (021) 5102681.

1990 Science for Art Prize

The Moët Hennessy Science for Art Prize (FF100K) is dedicated to promoting remarkable scientific initiatives which could stimulate creativity in fields where the expected interaction of art, science and industry may occur, and therefore could widen the scope of aesthetic creativity to the scientific field. The theme for 1990 of the Science for Art Prize is:

Application of Matter on a Surface — "Physicochemical phenomena, processes of deposit and aesthetic effects."

For further information contact: Moët-Hennessy ♦ Louis Vuitton, Direction du Développement, 30, avenue Hoche, 75008 Paris, France.

Products

Alusec — Manchem

Manchem have asked us to point out that the development and production of the Alusec range of high solids cross-linking systems wrongly attributed to the Mooney Chemical Co on p430 of November 1989 JOCCA is in fact the development product of Manchem.

**FEBRUARY
JOCCA:
J-i-T**

New acrylic emulsions development

Scott Bader Company Limited have completed a four year major research project to develop new acrylic emulsions for paints. The project was directed at providing new technology for both colloid and surfactant stabilised latices, with enhanced wet adhesion to difficult surfaces such as wood and alkyd gloss paint.

For further information Enter A201

New Resimene crosslinkers

The Resins Division of Monsanto Company has announced the introduction of eight new Resimene Crosslinker resins for the paint and coatings industry. These new products are targeted for automotive, coil, wood furniture or general metal coatings. They are designated: Resimene CE-6550, Resimene CE-6517, Resimene 2040, Resimene CE-4518, Resimene CE-4514, Resimene HM-31-328, Resimene AQ-7550 and Resimene HM-7531.

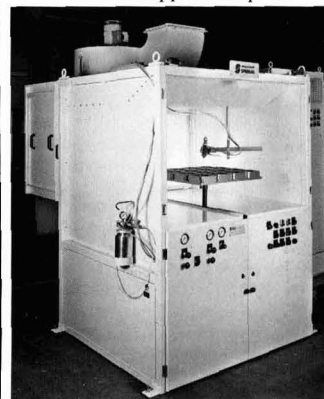
For further information Enter A202

Equipment

New automatic spray painting machine

Sprimag have introduced a programmable three-axis spray painting machine for the spray painting of plastic parts up to 800mm wide. In the basic stage, programs for 50 different parts can be stored.

The machine applies the paint



coats horizontally and crosswise like a hand sprayer, the four most critical parameters are stored in an SPS control: gun speed, spraying start and end for each reciprocating motion, as well as spraying start and end for each part to be painted, and further the feed rate of the workpiece holder. The basic equipment of the automatic spray painting machine comprises the sprystation with gun, exhaust system, paint supply system and SPS control, as well as the automatic feed device, with the workpiece holder moving into the loading or unloading position outside the sprystation.

For further information Enter A203

Recipe system with the right ingredients



The Stevens 3700 Recipe System allows both minor ingredients (RHS) and bulk discharge material (LHS) to be accurately formulated by one person from a single control unit.

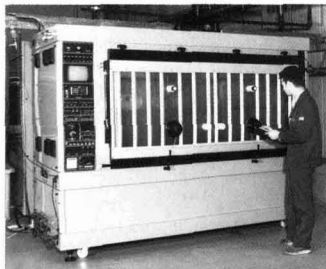
The simple operation of their new 3700 Recipe Formulation System, helps achieve a perfect mix from up to 12,000 recipe/ingredient combinations, claim Stevens AWS Ltd. Whether weighing out small quantities manually into buckets, or controlling automatic, multi-silo discharges, the 3700 provides greater accuracy, correct sequencing, efficient materials handling and better management control.

For further information Enter A204

New environmental test chamber

John Godrich have introduced the latest Liebisch Combined Corrosion/Environmental Test Chamber. The model KTS-2000 is a 2000 litre capacity test chamber over 2 metres long internally, with a front opening door and is controlled via a computer with a video screen

to give components tests to the effects of salt, humidity, dry heat, fresh air with options of sulphur dioxide. The unit is complete with salt spray conditions ASTM B117, humidity with a range of 30 up to 98% (controlled), dry heat up to 60°C (with a final low humidity), fresh air option and facilities for sulphur dioxide testing should these be required. All of the above is controlled via a computer mounted in the machine which allows individual programming in several different modes.



For further information Enter A205

Two new calorimeters

Two calorimeters have been introduced by Roth Scientific. Both calorimeters are designed to measure heat changes accurately for a wide variety of materials. The C80 calorimeter is a versatile unit offering controlled temperature rises from ambient to 300°C with a heat detection limit of 10µW; while the BT215 is more sensitive at 2µW and is particularly suitable for low temperature investigations between -196°C and +200°C. Typical applications of the C80 include measuring the curing temperature of an epoxy resin.

For further information Enter A206

Literature

Literature Miscellaneous

Phillips new catalogue on electrochemistry equipment

For further information Enter A207

'US MIL Specs — 40,000' and '1990 Catalogue of American Standards' from ILL.

For further information Enter A208

Synthetic latex polymers in Western Europe

In a 500-page report Kline analyzed the market for 17 of the most commercially important synthetic latex polymers across 15 industry areas. Western Europe in 1987 consumed an estimated 1.28m dry tonnes of synthetic latex polymers and emulsions, valued at an estimated DEM 4.5b. Growth at 3.5% per year was above industry average.

In 1987, the paints, coatings and construction industries accounted for 25% of all synthetic latex polymers consumed in Western Europe. The paper industries consumed about 22%, adhesives and sealants and carpet 16% each. While integrated latex and emulsion suppliers dominated the market in 1987 in Western Europe, there are still opportunities in the market open to independent producers.

At least 85 companies for either merchant sales or captive consumption have been identified. The five largest latex types accounted for nearly 80% of the tonnage demand in 1987. The first five latex suppliers accounted for nearly 50% of the total amount of latex sold in 1987.

Outlook: Synthetic latex polymers are forecast to grow from about 1.2m dry tonnes valued at DEM4.5b to about 1.55m dry tonnes valued at DEM4.7b in 1992, an average annual growth rate of 3.5%. According to the Kline report carboxylated butadiene-styrene, ethylene-based pressure polymer emulsions and polyurethane dispersions will do particularly well. Polyvinyl acetate homopolymer emulsions, however, will show low growth. Some commodity latices will show growth rates up to 5.5% a year. Medium sized speciality sectors can reach also 20.5% annual growth rate.

The report "Synthetic Latex Polymers — Western Europe 1988" is available on subscription from Kline.

For further information Enter A215

Infrared Spectroscopic Atlas of Polyurethanes.

SFR 209. Technomic Publishing.

For further information Enter A209

Inorganic Reactions and Methods.

18 vols. VCH.

For further information Enter 210

DTI QA Register. Subscr. £125.

HMSO.

For further information Enter 211

Chemical and Industrial Consultants Association Directory.

£10. CICA, UK.

For further information Enter 212

The free leaflet "Introducing the Noise at Work Regulations"

(IND(G)75(L) is available from HSE Public Enquiry Points at London (01-221 0870); Sheffield (0742) 752539); and Bootle (051-951 4381).

Industrial Research in the UK Longmans 1989. £15.00, 3,400 entries.

For further information Enter A213

ICC Business Ratio Report — Paint and Printing Ink Manufacturers — 18th Edn. 1989. £225.

For further information Enter A214

Radiation Curing of Polymeric Materials. ACS Symposium Series No. 417. 1989. \$119.95.

For further information Enter A216

Chem-Facts UK, FRG, Holland, Belgium — Chemical Intelligence Services. £180/vol.

For further information Enter A217

Guidelines for the Technical Management of Chemical Process Safety. Clark Associates — Europe Ltd. £80. 224pp.

For further information Enter A218

HSE RPE list

The Health and Safety Executive (HSE) has published free of charge a preliminary document listing type approved respiratory protective equipment (RPE) and lists of approved standards for RPE. The lists cover equipment ranging from filtering facepiece respirators to breathing apparatus which may be needed under the COSHH Regulations. The lists are published in "RPE — Legislative Requirements and Lists of HSE Approved Standards and Type Approved Equipment", which is available from HSE Enquiry Points

in Bootle (051-951 4381), Sheffield (0742 752539), and London (01-221 0870).

Meetings

Academia-industry links

A one-day seminar on the Industry File for Chemistry organised by Oakland Consultancy will be held on 30 January 1990 at the Strand Palace Hotel, London. The Seminar will explore new ways of promoting links between higher education and industry. For further information contact: Kim Cross, Oakland Consultancy Ltd., 73 High Street, Girton, Cambridge, CB3 0QD.

Slurry handling seminar

Warren Spring Laboratory is holding a one day seminar on Slurry Handling on 1 February 1990, £150+VAT. For further information contact: Carolyn Abel, Warren Spring Laboratory, Gunnels Wood Road, Stevenage, Herts SG1 2BX.

TiO₂ global outlook

A three-day international conference titled "The Global Outlook for TiO₂ and TiO₂ Replacements/Extenders" will be held on 18-20 March 1990 at the Stouffer Concourse Hotel in St. Louis, Missouri. For further information contact: Conference Services, Falmouth Associates Inc., 170 U.S. Route One, Falmouth, Maine, 04105 U.S.A. (Telephone 207-781-3632, Fax 207-781-4177).

University of Bradford

Classification and sorting of solids 27-29 March, Two-phase separation with cyclones 9-11 April, On-line monitoring of particle size 16 May (Ldn), Solid-liquid separation 11-14 September, Particle size measurement and sampling 18-20 September, Bulk powder testing 25-27 September. For further information contact: Dr. L. Svarovsky, Chem. Eng. Dept., University of Bradford, Bradford, West Yorks, BD7 1DP.

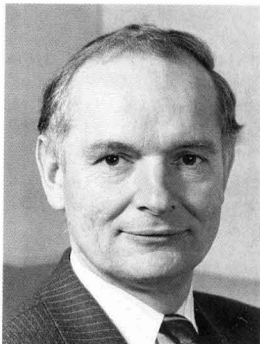
Corrosion — Five Star Rating

Staff at the Corrosion and Protection Centre, UMIST, are justly delighted about their recent five star research rating carried out by the University Funding Council. This quality team plus renowned experts from industry offers two one-week courses in 1990 in Spring, 2-6 April and Autumn, 24-28 September. In April, there is the unique, firmly established Corrosion Engineering and Control Course. For further information contact: David Scantlebury, The Corrosion and Protection Centre, UMIST, PO Box 88, Manchester M60 1QD, Tel: 061-200 4841, Fax: 061-200 4865.

People

Macpherson PLC

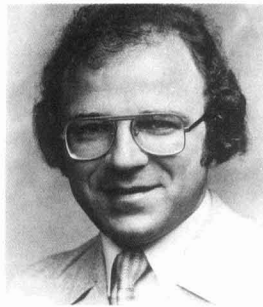
Brian R. Parks has been appointed Chief Executive of the Macpherson PLC group of companies which has a turnover of approximately £100m and includes one of the United Kingdom's biggest paint manufacturers and leading names in the production of polymers, resins, industrial and wood finishes. Mr Parks, 48, has been with the Group since 1986, first as Managing Director of Macpherson Drynamels until its disposal a year later and then as Managing Director of Macpherson Polymers at Birch Vale, near Stockport, where he has controlled two manufacturing sites with sales in the region of £20m and a workforce of 130.



B. R. Parks

Jotun Polymer (U.K.) Ltd

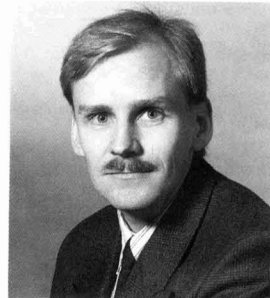
Chris M. Sghibartz has been appointed Managing Director of Jotun Polymer (U.K.) Ltd. Jotun Polymer (U.K.) Ltd. is a fully owned subsidiary of Jotun Polymer A/S of Norway, a leading European manufacturing and marketing company for unsaturated polyesters, gelcoats and trade goods for the reinforced plastics industry. Dr Sghibartz, 39, a chemistry graduate of Imperial College London, carried out postgraduate studies at King's College London and joins Jotun Polymer (U.K.) Ltd after almost 4 years as Business Development Manager with the Corporate Development Department of RTZ Chemicals Ltd in London.



C. M. Sghibartz

Chemoxy International

Ian Dell has been appointed Business Development Manager of Chemoxy International. His role will include the development of chemoxy's custom processing business and marketing of the company's low toxicity solvent Estasol. Ian joins the company from Huls UK/Dynamit Nobel.



I. Dell

Synthetic micaceous iron oxide: A new anticorrosive pigment

by E. V. Carter and R. D. Laundon*, Cookson Laminox Ltd, Mill Hill, North West Industrial Estate, Peterlee, Co. Durham SR8 2HR, UK

Abstract

A process has been developed to synthesise lamellar iron oxide for use as a pigment in protective coatings for steelwork. Chemical and physical characteristics can be controlled to achieve optimum performance capabilities. Two grades of pigment have been produced in pilot plants, a synthetic micaceous iron oxide for use in top coats and a finer version for priming paints. Evaluations in a range of paint formulations have demonstrated superior anticorrosive properties compared with traditionally used pigments. The construction of a bulk manufacturing plant is nearing completion.

Introduction

Anticorrosive pigments are frequently described as either active or inert depending on their particular function within a paint film.

Active pigments are used mainly in primers to take part in chemical or electrochemical processes to inhibit corrosion at the steel interface. Well-known examples are red lead, zinc chromate, zinc phosphate and zinc dust.

Inert pigments depend mainly on their physical characteristics to enhance the barrier properties of the coating. Permeability to water and oxygen is reduced and resistance to ionic transmission through the coating is increased. Micaceous iron oxide (MIO) is arguably the most important pigment in this class. MIO is a metallic grey, lamellar form of Fe_2O_3 , and depends on its flake-like particle structure to produce the barrier effect. For many years, MIO pigment has been obtained from beneficiation of crude iron ores.

Attempts to synthesise MIO in the past have failed to yield little more than laboratory samples but a completely new process has now been developed which has produced working quantities of pigment with optimised chemical and physical properties. Bulk production of the new synthetic MIO is scheduled to commence this year.

The use of MIO pigment in anti-corrosion coatings for steelwork started in Britain about 90 years ago and eventually spread into Europe and many Commonwealth countries. In the early days, MIO paints were employed extensively on bridges and viaducts built for the railway systems that were growing rapidly at the time. Their use extended to include motorway bridges and a wide variety of other types of engineering structures, large and small. Traditionally MIO has been used mainly in undercoats and finishes in conjunction with compatible primers. Pigmentation of anticorrosive primers with MIO is less common.

Initially MIO was incorporated into oil based binders, sometimes modified with natural resins. A typical protective paint system 50 years ago consisted of red lead primer overcoated with oleoresinous MIO undercoat and finish. Over the years, more technically advanced binders became available and many of these have been adopted for MIO paints, e.g. phenolic resins, modified alkyds, chlorinated rubber, vinyl copolymers, epoxies and polyurethanes^{1,2}.

Mechanism of protection

The protective properties of MIO are ascribed to the close-packing of pigment platelets within the paint film, forming overlapping layers positioned approximately parallel to the substrate plane³. At optimum pigment volume concentration (PVC) the pigment layers form a barrier which impedes permeation of moisture and corrosion-stimulants (such as chlorides and sulphates) and increases the ionic resistance. The pigment flakes also produce a reinforcing and stress-relieving effect resulting in enhanced cohesion and film integrity. When exposed to strong sunlight, UV degradation of the binder is much reduced because the iron oxide platelets lying on the upper surface, strongly absorb radiation of wavelength 300-400nm and effectively shelter the organic molecules underneath from photo-chemical attack. (See Figures 1-4).

Evaluations and tests on a range of MIO pigments conducted in a number of laboratories have shown that the particle shape and size characteristics greatly influence the protective properties and durability in coatings⁴⁻⁶. It has also been well demonstrated that there are significant divergencies in properties between the different qualities of MIO pigments currently available from natural sources.

Natural MIO pigments

Natural MIO is obtained from mineral deposits of specular haematite found in various locations including Austria, (the main source), Spain, South Africa, Japan, Australia and India. Pigments obtained from these deposits vary considerably in morphology, physical characteristics and chemical purity. Microscopic examination of several commercial pigments reveals that the particle shape can range between flake-like (varying between thin flakes and thick flakes) and completely granular. Some of the pigments consist of a mixture of many different shaped particles. An extremely good quality MIO pigment, containing a high proportion of lamellar particles used to be mined in South Devon but the deposit became exhausted 20 years ago. This pigment contained platelets 10-75 μm in diameter with a flake thickness mainly below 5 μm . It possessed outstanding protective properties and earned a first class reputation from the early 1900's onwards. In developing a new synthetic MIO in our laboratories we considered the original English grade pigment to be the minimum standard to aim for.

National and International standards are unhelpful in establishing requirements for MIO pigment. The current British Standard for iron oxide pigments BS 3981-1976, (ISO 1248-1974) includes a section for MIO but although it explains that micaceous iron oxides should have a lamellar form, there are no tests or criteria for pigment particle shape. This is in contrast to the previous BS 3981-1966 which included a method for assessing the lamellar nature of MIO by means of a water-covering area test similar to that used for aluminium flake. For many years, technologists have checked the flake-like properties of MIO by viewing the pigment under an optical microscope (x150-200) by transmitted light.

* Dr Laundon is now with the Harcros Chemical Group.

Figure 1

Conventional pigments have only limited barrier properties and allow penetration of ions.

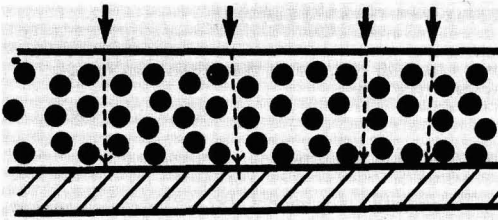


Figure 2

Lamellar pigments packed in layers lengthen the pathways and obstruct penetration of ions.

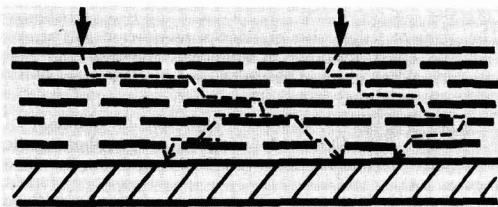


Figure 3

Spherical pigments allow UV to attack the organic binder causing erosion.

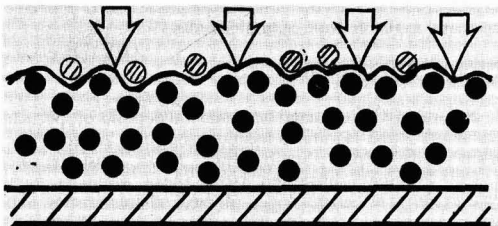
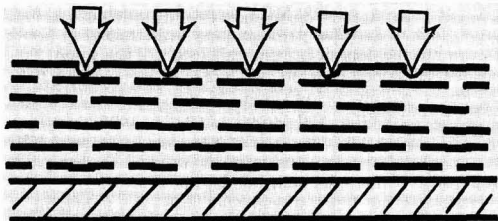


Figure 4

Overlapping platelets of iron oxide at the surface absorb UV radiation and protect the underlying binder.



Using this technique, flakes with thickness below about 5µm show up as sharply-defined ruby red translucent crystals while thicker flakes or granules appear as black blobs. This type of test has been included in Australian Standard AS 2855-1986 and it is hoped that a future BS/ISO standard might incorporate something similar.

Synthetic micaceous iron oxide

There are obvious technical advantages to be gained from

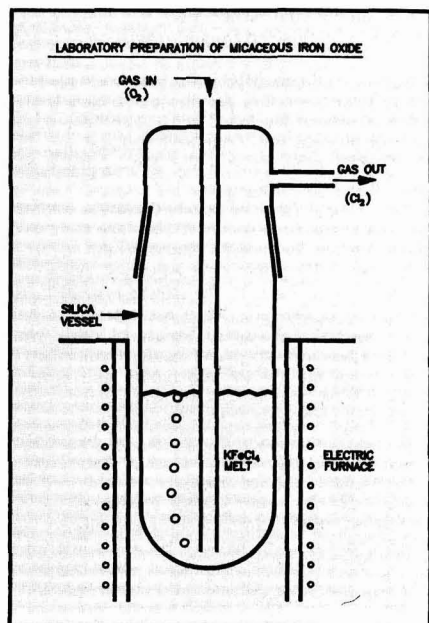
making MIO pigment by synthetic means. One can select those desirable characteristics possessed by the natural pigment which enhance the long term durability and corrosion resistance of coatings and faithfully reproduce them. Or better still, improve upon them and increase the performance capabilities. One can also eliminate those faults and undesirable properties inherent in natural pigments caused for instance by adventitious matter and impurities. A very important benefit in these days of preoccupation with BS 5750 and ISO 9000, is that all the required properties and characteristics can be maintained within predetermined and agreed standards.

The overriding constraint of course, as always, is cost. Is it really possible to manufacture a synthetic MIO and sell it at a price that will compete effectively in the market place with traditional products obtained by simple beneficiation of natural minerals? (Or as a Liverpudlian wag once put it; "shovelling it out of the ground into bags"). This is essentially the same question that faced colour chemists 60 years ago when they dared to synthesise the iron oxide pigments that seemed to make up most of the earth's crust in Spain and many other places. We are told now, that much more synthetic iron oxide is purchased by the paint and building-products industries than the natural oxide, even though the latter is cheaper! Marketing studies have indicated that it is indeed possible to compete effectively and provide good value for money with a very technically advanced product.

There have been many attempts to synthesise MIO over the last 25 years or so but they never became commercial because of the high costs involved. Two basic methods were employed, hydrothermal transformation of $\text{FeO} \cdot \text{OH}$ in an autoclave and the oxidation of molten salt complexes such as KFeCl_4 at high temperatures^{7,8}. There were a considerable number of technical and economic problems associated with

Figure 5

Preparation of synthetic MIO by heating a mixture of anhydrous ferric and potassium chlorides at 700°C and bubbling oxygen into the resulting molten KFeCl_4 complex. Platelets of Fe_2O_3 form as a precipitate.



scaling up these methods to production levels so they never progressed much further than the laboratory bench. (See Figure 5).

Early work in our laboratories at Teddington, next door to the PRA, concentrated on improving the molten complex oxidation techniques to produce lamellar crystals of pure iron oxide. Anhydrous iron chloride was made directly by reacting metallic iron with chlorine gas, simultaneously converted into molten complexes with common salt and then oxidised with air, all at high temperatures. Further developments concentrated on making the process more efficient and reproducible⁹. The process equipment was progressively modified and improved and went through evolutionary stages with yields of pigment per batch increasing from 70 gms to 70 kgs.

A production plant to manufacture synthetic MIO is currently under construction, the first phase of which is planned to come on-stream during early 1990.

The chemical process

The chemical reactions involved in the process are shown below and can be separated into three stages:

Stage 1	Chlorination
$2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3$	(1)
$\text{Fe} + 2\text{FeCl}_3 \rightarrow 3\text{FeCl}_2$	(2)
$2\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3$	(3)
Stage 2	Complexation
$\text{FeCl}_3 + \text{NaCl} \rightarrow \text{NaFeCl}_4$	(4)
$\text{FeCl}_2 + \text{NaCl} \rightarrow \text{NaFeCl}_3$	(5)
Stage 3	Oxidation
$4\text{NaFeCl}_4 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{NaCl} + 6\text{Cl}_2$	(6)
$4\text{NaFeCl}_3 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{NaCl} + 4\text{Cl}_2$	(7)

A novel chemical reactor, was developed in which metallic iron is converted to MIO by the above chemical reactions in a single operational stage. Suitable sources of iron are scrap steel turnings and punchings. High conversion rates are achieved by oxidising thin films of the molten salt complex spread over the surfaces of lumps of refractory material packed inside the reactor. Handling of chlorine gas is facilitated and its consumption minimised by a system of internal recycling within the reactor.

The reactor comprises a cylindrical steel shell lined with refractory with lids fitted at the top and bottom, gas inlets at the base and a gas outlet at the top. The reactor is charged by filling with a shallow support layer of refractory pieces, (which act as a gas distributor) followed by a deeper layer made up of a mixture of scrap iron, salt and refractory pieces. (See Figure 6).

Reaction is initiated by pre-heating the base of the charge to approximately 700°C and then passing a mixture of chlorine and air into it. The sequence of chemical reactions is outlined in Figure 7. Chlorine reacts with the pre-heated iron and salt to form a reaction zone and a film of NaFeCl₄ is formed on the surfaces of the refractory support. Sufficient chlorine is introduced to produce a reaction zone which is only a fraction of the total height of the charge layer. Air is fed to the reactor and the oxygen reacts with the molten NaFeCl₄ to form lamellar iron oxide crystals encapsulated in a layer of salt, releasing chlorine gas. Chlorine from the first zone travels up the reactor to form a new reaction zone, which is in turn oxidised by the air. Thus the reaction zone moves gradually upwards until eventually chlorine is evolved from the top of the charge. This internal recycle process considerably reduces the amount of chlorine needed and in

fact only about one tenth of the stoichiometric quantity is required. The reactions are exothermic and self-sustaining in energy, once initiated.

When reaction is complete the charge is let out from the bottom of the reactor. The salt layer is dissolved off the refractory support and the synthetic MIO is collected on filters, washed free of chloride, and dried. By adjusting the reaction conditions, different sizes of MIO crystals can be produced. This makes it possible to form flakes of varying thickness from 0.5-5µm (or more) and "diameters" from 1-100µm.

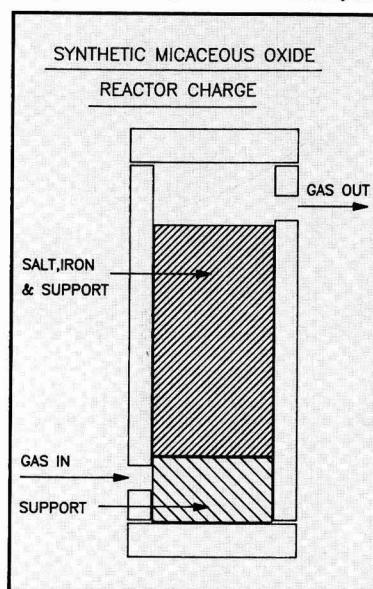
This process is protected by patents worldwide.

Typical properties of synthetic MIO are as follows:

Iron Oxide content	97.5% Fe ₂ O ₃
Specific gravity	5.0
Volatile content (105°C)	0.11%
Water soluble matter	0.06%
pH of aqueous extract	7.2
Soluble chloride	0.01%
Soluble sulphate	0.01%

Figure 6

Diagrammatic sectional view of reactor. The support on which the reactions take place consists of pieces of inert refractory material.



Evaluation of synthetic MIO in paints

Several thousand kilograms of synthetic MIO were produced on a pilot plant enabling a wide-ranging evaluation programme to be carried out. By altering the reaction parameters, the morphology of the iron oxide particles could be varied¹⁰. The ability to tailor-make the pigment to almost any particle shape and size posed some important questions. What is the best particle size distribution and flake thickness? Should it be the same as the natural pigment or could it be improved? Several published studies of MIO pigment have emphasised that a "thin-flake" particle shape is essential for good performance¹⁻⁶. Examination by scanning electron microscopy of commercial MIO pigments revealed that the flake thickness even of acceptable lamellar material varied

from 4-10µm or more. Several grades had particles well above 10µm thickness to the extent that they could not really be described as lamellar. It was possible to obtain exceptionally thin flakes by the synthetic process. These were capable of almost ideal leafing and parallel orientation within paint films but unfortunately they were the wrong colour; more like burnished copper than the familiar steel grey! We decided that the optimum flake thickness was around 2-5µm, similar to the original English natural MIO. A comparison of scanning electron micrographs of a currently available natural MIO and synthetic MIO is shown in Figures 8 and 9.

A selected particle size distribution could be obtained by

Figure 8

SEM (x500) of natural micaceous iron oxide pigment. Particle characteristics and quality derive from the basic crystalline structure and composition of the crude ore from which obtained.

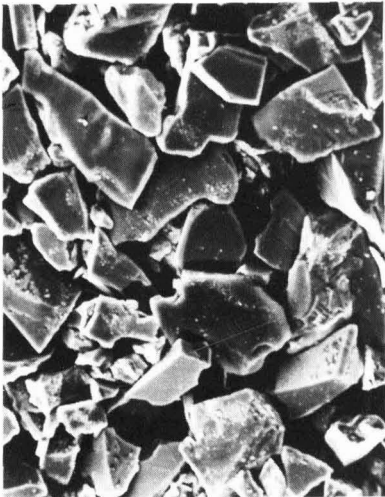
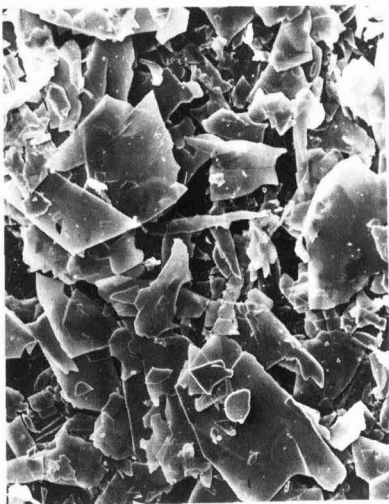


Figure 9

SEM (x500) of LAMINOX synthetic MIO. The flake-thickness and particle size range are controlled within precise limits to produce optimum properties.



controlling the crystallisation process in the reactor and by subsequent classifying methods to remove unwanted fines and oversize fractions. The proportion of fine particles and very thin flakes had a pronounced effect on the colour of the pigment. For instance, increasing the content of "fines" produced redder undertones.

From a series of evaluations done with assistance from the paint industry, we concluded that the particle size range should be pitched lower than most commercial natural MIO pigments i.e. even finer than the so-called airless spray grades. This greatly improves pigment-dispersion, reduces tip-blocking and minimises imperfections in the dry film.

Initial tests on synthetic MIO were conducted on samples made with three different particle size distributions in order to decide on optimum levels having regard to both visual appearance and anti-corrosion capabilities. Laboratory test programmes were carried out by end-user organisations and paint manufacturers as well as ourselves. Exposure tests at various exterior sites were also arranged¹¹.

The synthetic pigments were made up into typical MIO paint formulations based on a range of binder types (see Table 1) at optimum pigment volume concentrations, mostly in the region of 30-40% and tested by the methods listed in Table 2. For comparison purposes, parallel tests were conducted on paints similarly pigmented with natural MIO.

Table 1

Binders used in MIO tests

- Long oil alkyd.
- Urethane oil/alkyd.
- Chlorinated rubber.
- Vinyl copolymers.
- Vinyl acrylic copolymer (water thinned).
- Styrene acrylic copolymer.
- Epoxy-polyamide.
- Polyurethane.

Table 2

Test methods for comparing synthetic and natural MIO

- Water vapour permeability.
- Water absorption.
- Salt spray (BS 3900/F4).
- Accelerated weathering (BS 3900/F3).
- BR77 cycling salt spray (British Rail).
- Exposure to natural weathering in coastal, industrial and urban environments.

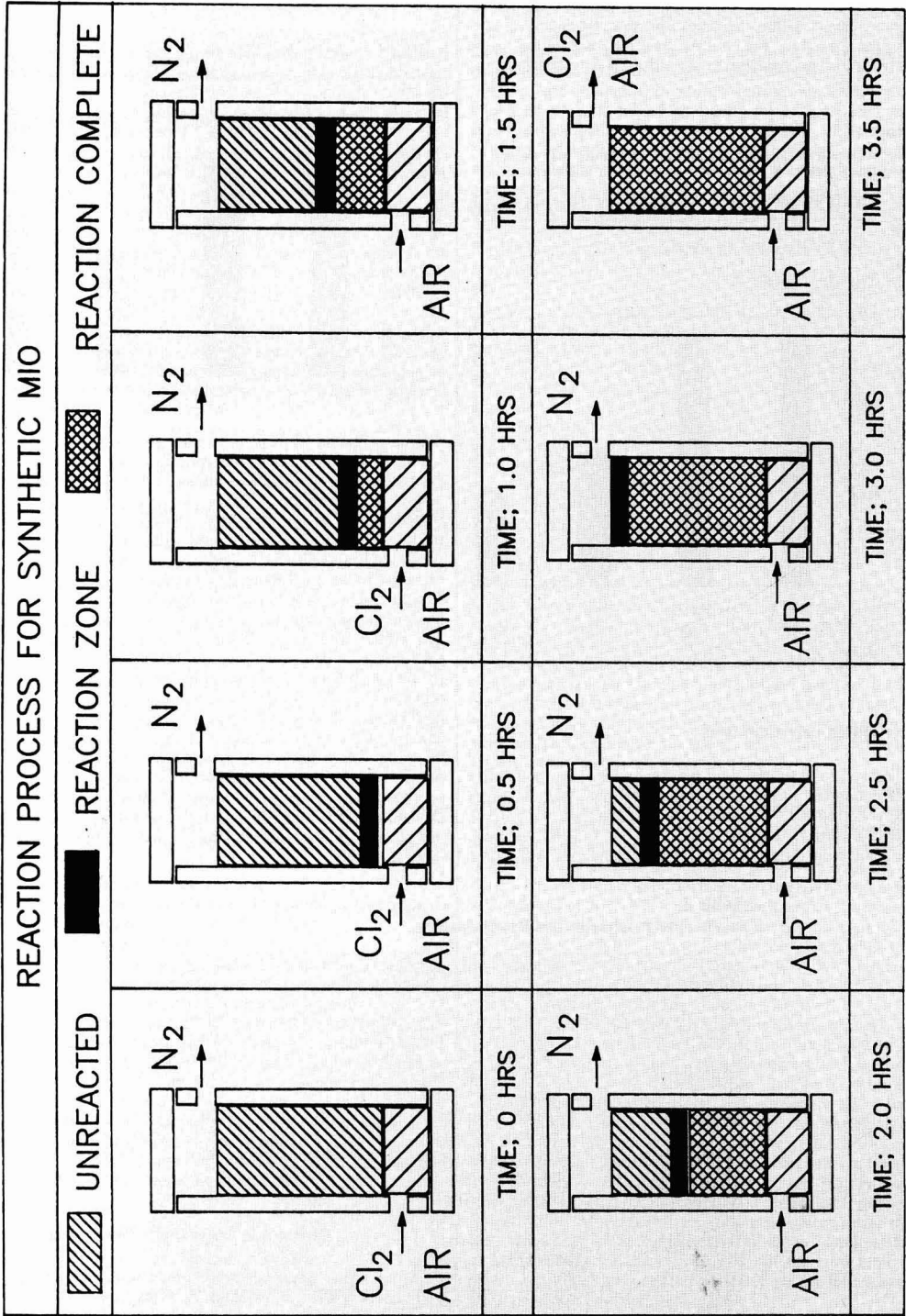
Much of this evaluation work has been completed although final results are still awaited on long term weathering trials. The overall conclusions that emerged from all these evaluations were that the synthetic MIO grades had first-rate protective properties and came well up to expectations. At the very least they matched up to the best quality natural products currently obtainable. However, in many of the tests, the synthetic grades were markedly superior to the natural pigment. Examples of some of these tests are given below and fuller details of more wide-ranging tests are to be published in a future paper.

Following these initial assessments, particle diameters of the synthetic MIO were optimised to fall within a 5-75 micron range with a 3-4% retention on a 63 micron sieve and this grade of pigment has been named LAMINOX S. Another grade with a much finer particle size range has also been developed for use in priming paints and is discussed later.

Permeability and absorption determinations

Synthetic MIO grades in alkyd binder had lower water-vapour permeability when tested by Payne cup techniques.

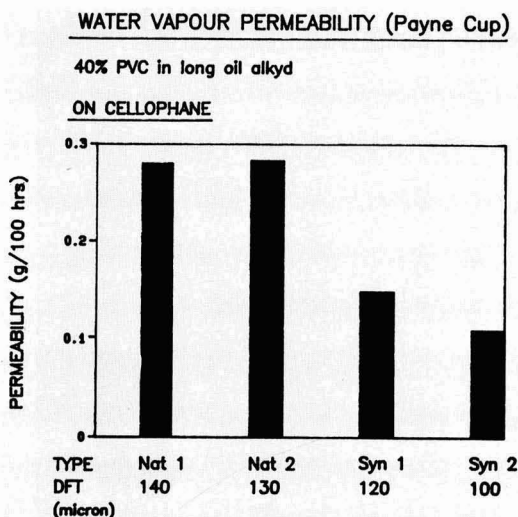
Figure 7
 Progress of reactions in the production of synthetic MIO.



(See Figure 10). They also had lower water-absorption properties when applied to glass slides and immersed for 7 days. (See Figure 11). These tests indicate that the thin-flake particles of synthetic MIO permitted tighter packing of pigment layers within the paint film thus producing a more efficient barrier. The better packing capabilities were confirmed by microscopic examination of cross sections.

Figure 10

Water-vapour transmission rates of paints pigmented with natural and synthetic grades of MIO. (DFT = Dry Film Thickness).



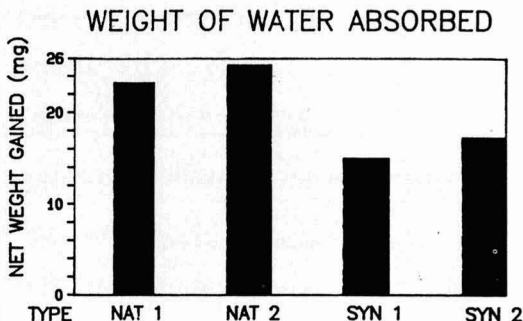
Accelerated corrosion tests

Tests on some earlier pilot-plant samples of synthetic MIO were conducted in the laboratories of British Rail Research and Development division¹⁰. Three synthetic pigments (A,B,C), with a particle size range of 0.5-100 microns, (distributed in different ways,) were compared with three

Figure 11

Water absorption properties of alkyd paints pigmented with natural and synthetic grades of MIO. Paint films (approx. 330 mgs) were cast on glass slides and immersed for 7 days.

WATER ABSORPTION TESTS MIO/ALKYD



natural pigments (D,E,F) of similar particle size range.

Paints were prepared incorporating each of the MIO samples in a urethane-alkyd binder with a nominal pigment volume concentration of 35%. One coat of each paint was brush-applied to abraded steel panels at 50µm wet film thickness. Each panel was scored with a diagonal cross and subjected to the BR77 salt spray test, i.e. cycles of four hours exposure to salt fog followed by one hour drying out at room temperature. Salt solution composition was 0.41% ammonium sulphate and 0.031% sodium chloride in water. The panels were exposed for a total period of 683 hours except for one coated with natural MIO paint (D) which had to be withdrawn prematurely because of the rapid breakdown. The results are summarised in Table 3 the performance ranked on the basis of a visual assessment of the amount of corrosion staining over the painted surfaces. The paint film was subsequently stripped from one quarter of each panel to determine the extent of corrosion of the steel substrate. The conclusions drawn by British Rail R and D Division were that the particle size distribution and morphology of the pigments had a major influence on the relative results.

Table 3

Results of BR77 salt spray tests on MIO pigments

MIO Grade*	Particle Characteristics: Size Range 0.5µm - 100µm	% Corrosion on:	
		Paint Surface	Bare Steel
Synthetic (B)	High Proportions of finer particles	0	Few spots
Synthetic (A)	Even distribution. Mainly below 75µm	5-10	5
Natural (F)	Mainly lamellar. Even distribution.	40	30
Synthetic (C)	High proportion of larger particles.	100	60
Natural (E)	Mainly lamellar. Even distribution	100	60
Natural (D)	Mainly granular. Even distribution	100	90

(failed rapidly)

* Ranked in descending order of corrosion protection

A new pigment for anticorrosive primers

Discussions with paint technologists frequently elicited the question; "Can you make a special MIO suitable for use in anticorrosive primers?". The need for environmentally acceptable anticorrosive pigments to replace those based on lead and chromates in priming paints has stimulated the emergence of phosphate, molybdate and borate based inhibitive pigments and many others. However there are widespread doubts about the ability of these "non-toxic" alternatives to provide the same degree of corrosion-resistance as the lead and chrome pigments. This has encouraged a search for ways and means of boosting the inhibitive action of the newer pigments, by mixing with other ingredients that might promote a synergistic effect. There has been a growing interest in utilising inert barrier pigments for this purpose, especially those with a lamellar particle structure. The combination of flaky pigments with inhibitive pigments in primers is not a new idea. Many years ago graphite was extensively used in conjunction with red lead to improve weather resistance. Non-leaving aluminium was recommended as a component with basic lead sulphate in an alkyd primer that was much favoured by the British Iron and Steel Research Association¹².

More recently, micaceous iron oxide has been utilised in high-build zinc phosphate primers and has performed very successfully on structural steelwork². However, the appreciable content of fairly coarse particles in conventional MIO pigment has limited its scope for use in anticorrosive primers and it is more commonly restricted to undercoats and finishes. Natural MIO pigment with its particle size range of 5-100 μm (typically having a residue of up to 15% on a 63 μm sieve) also contains a significant amount of non-lamellar particles. Therefore, conventional MIO is at its best in primers only when they can be applied at a sufficiently high film build. In thinner coatings, e.g. below 50 μm , the larger sized granular particles tend to form connecting links between the paint surface and the substrate, creating pathways for penetration of moisture and corrosion stimulants¹³. Another disadvantage with natural MIO is that some qualities contain sulphide impurities which under certain conditions can oxidise to sulphates and encourage corrosion cells to form at the steel interface⁴.

It could be said that an ideal barrier pigment for primers should have the following characteristics:

1. A high content of lamellar particles, the thinner the better.
2. Particle size range below 20 μm .
3. Free from impurities that could encourage blistering or stimulate corrosion.
4. Low chemical reactivity, i.e. inert.

Such an ideal pigment would be broadly similar to a high quality MIO but with all the impurities removed and possessing a much finer particle size distribution.

It is now possible to produce such a unique pigment from the synthetic MIO process. Finer particles than those making up the bulk of conventional MIO, can easily be obtained by adjusting the process conditions. The new pigment has been found to have considerable potential for enhancing the anticorrosive properties of primers and has been given the trade name LAMINOX F. In appearance the pigment is redder than conventional micaceous iron oxide and might be described as purple-brown or purple-grey.

Comparisons with traditional iron oxides

Although it has the same chemical composition, (Fe_2O_3), the new lamellar pigment is different in many respects from the familiar synthetic red iron oxides that are manufactured in

the sub-micron particle size range. As we all know, synthetic red iron oxides are frequently included in anticorrosive primer formulations in conjunction with zinc chromate, zinc phosphate etc., but they do not claim to have any inhibitive action and their barrier properties are very limited. Their main use is to improve opacity, film build and application properties and possibly to reduce material costs.

Tests were conducted in our laboratories on the fine grade lamellar iron oxide and a high quality synthetic red iron oxide (used as a standard for comparison) to study their relative barrier properties in primers. The synthetic red oxide is a well-known type used widely in association with inhibitive pigments. Both pigments had similar oil absorptions, (around 30.)

Each oxide was incorporated as the sole pigment to check the intrinsic barrier mechanism and also in combination with zinc phosphate (at two levels) to explore possible synergistic effects. In the first test series, we examined only zinc phosphate as the active pigment as it is the most widely used in the UK, but there are a number of other non-lead, non-chromate pigments available which also claim to give a high level of corrosion inhibition. Many of these will be examined in future evaluation programmes in admixture with the new pigment.

To keep the evaluation as simple as possible, a solvent based alkyd was used as the binder and four basic formulations were employed as follows:

- a. Iron oxide used as the principal pigment: PVC = 40%
- b. Iron oxide used as the principal pigment: PVC = 30%
- c. Zinc phosphate/iron oxide mixture. Ratio = 3:5
PVC = 35%
- d. Zinc phosphate/iron oxide mixture. Ratio = 5:3
PVC = 33%

The paints were brush-applied at a dry film thickness between 35-40 μm on to abraded steel panels in single coats and allowed to stand for 7 days before testing. Panels were exposed to continuous cold salt spray (BS 3900/F4) for varying periods and the appearance of the painted surfaces noted. At the end of the test period, the coating was removed with paint stripper from half of each panel and the underlying steel surfaces examined to assess the extent of corrosion. Details of the results are given in Table 4.

It was obvious from these tests that the lamellar oxide exhibited pronounced barrier properties which were substantially better than those of conventional red iron oxide. When used as the sole pigment at 40% PVC, the lamellar oxide provided considerably greater protection than the red oxide. The difference in performance between the two oxides was reduced at 30% PVC but the superiority of the lamellar pigment was still very evident. As expected, inclusion of the iron oxides at 30% PVC i.e. well below the critical level, gave much better results in both cases than at 40% PVC. However it was noteworthy that the lamellar oxide at 40% PVC was markedly superior to the red oxide at 30% PVC.

In the case of the mixed oxide/phosphate primers, the anticorrosive properties were enhanced substantially by the inclusion of lamellar oxide. In fact, the paint with 3 parts zinc phosphate and 5 parts lamellar oxide had better corrosion resistance than that with 5 parts zinc phosphate and 3 parts red iron oxide. This suggests that the zinc phosphate content can be almost halved, the remainder being made up with lamellar oxide, while still retaining adequate protective properties. Alternatively both the active pigment and lamellar oxide could be incorporated at optimised levels so as to achieve the best possible corrosion-resistance; better than that obtainable from either pigment alone. Optimisation would obviously call for careful study of the most effective pigment volume concentration required taking into account the type of binder employed.

In addition to the improvements that can be derived from

Table 4**Results of BS 3900/F4 salt spray tests — primers: Comparison of conventional and lamellar iron oxides**

Pigmentation†	PVC%	Appearance of paint surfaces after‡:			1500H	Condition of steel at end of period.
		500H	1000H	1000H		
RO	40	100% blistering 100% rusting	100% Coating completely disrupted	—	—	Rust nodules cover whole surface.
LF	40	No signs of blistering or corrosion.	A few blisters in centre. Some rust staining.	—	—	Corrosion blotches over ca. 20%
RO	30	About 25% blistering. No rust staining.	About 50% blistering. About 30% rusting.	—	—	About 50% corrosion evenly spread.
LF	30	No signs of blistering or corrosion.	A few isolated blisters. No rusting.	—	—	A few isolated rust spots.
ZP/RO 3:5	35	About 20% blistering. No rusting.	Fine blistering over-all. A few rust spots.	Extensive blistering. ca 20% rust staining.	—	50% corrosion evenly spread.
ZP/LF 3:5	35	No signs of blistering or corrosion.	No signs of blistering or corrosion.	Isolated blistering. A few rust spots.	—	One small patch of corrosion and a few rust spots.
ZP/RO 5:3	33	No signs of blistering or corrosion.	A few isolated blisters.	Fine blistering overall. A few rust spots.	—	30% corrosion spotting evenly spread.
ZP/LF 5:3	33	No signs of blistering or corrosion.	No signs of blistering or corrosion.	A few isolated blisters and rust spots.	—	A few isolated corrosion spots.

†RO = Synthetic red iron oxide, LF = LAMINOX F and ZP = Zinc phosphate.

‡H = Hours.

composite barrier/inhibitive pigmentations there are potential benefits to be gained from using lamellar iron oxide as the principal pigment in certain types of primer, eliminating active pigments entirely and utilizing the inherent barrier mechanism to obtain the anticorrosive properties. If required, the lamellar pigment could be incorporated at quite high levels i.e. approaching the critical pigment volume concentration and still provide good corrosion-protection. This is a distinct advantage for instance, when it is necessary to maximise adhesion between the primer and subsequent coatings, especially after a prolonged interval between applications e.g. as in the case of epoxy primers.

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Appendix

Notes on colour photographs

A few colour photographs are reproduced here to illustrate some of the points made in the paper.

The optical photomicrographs (x100) of MIO pigments (Figures 12-14) are by transmitted light. Thin-flake particles show up as red translucent platelets. Thicker flakes and granular particles have a much darker appearance. This simple test for lamellar properties has been proposed for inclusion in a new BS/ISO Standard for MIO.

To compare the protective properties of the new synthetic MIO (LAMINOX S) with the old established natural pigment, paints with identical formulations were made from the two pigments in a urethane alkyd binder. Two coats were airless sprayed onto degreased steel panels and onto blast-cleaned girder sections at equivalent film thicknesses. The MIO paints were applied directly over unprimed steel in order to assess the intrinsic barrier properties and to obtain accelerated results. Figure 15 shows the appearance of panels subjected to salt-spray and figure 16 shows the condition of girder sections after exposure to aggressive coastal conditions. Paint preparation, application and testing were all carried out by independent laboratories. In these and many other tests, superior protective properties were demonstrated by the synthetic MIO.

Figure 17 shows the results of a salt spray test on the finer grade lamellar pigment (LAMINOX F) compared with conventional synthetic iron oxide in anticorrosive primers. There are strong indications that the new pigment can boost the performance of zinc phosphate.

Figure 12

Photomicrograph of a natural MIO pigment that contains a high proportion of thin-flake particles. The colourless particles consist of silica and other minerals.

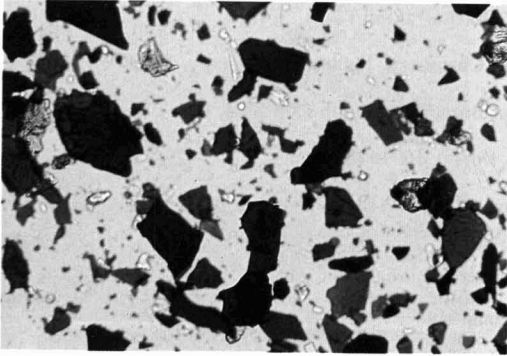


Figure 13

Photomicrograph of a natural MIO that contains a major proportion of thick-flake and granular particles.

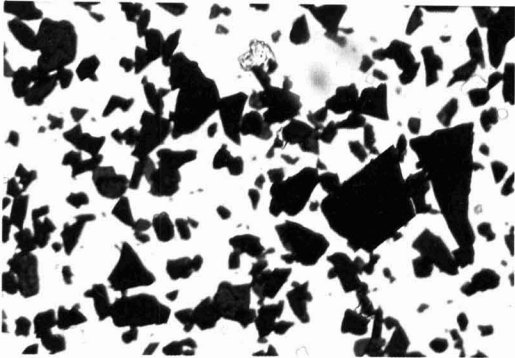


Figure 14

Photomicrograph of LAMINOX S synthetic MIO pigment with optimised flake structure.

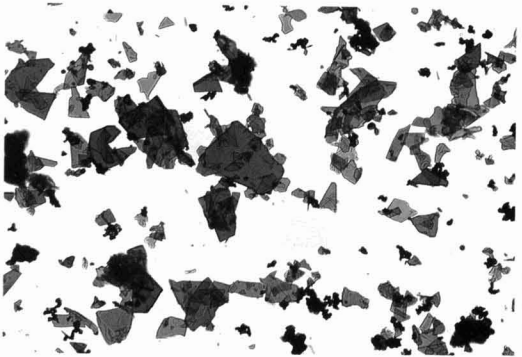


Figure 15

MIO painted steel panels subjected to BS 3900/F4 cold salt spray test. Natural MIO on the left; synthetic MIO on the right. Coatings were partially removed after 2000 hours to reveal the extent of corrosion. (Courtesy of Raccon Limited).

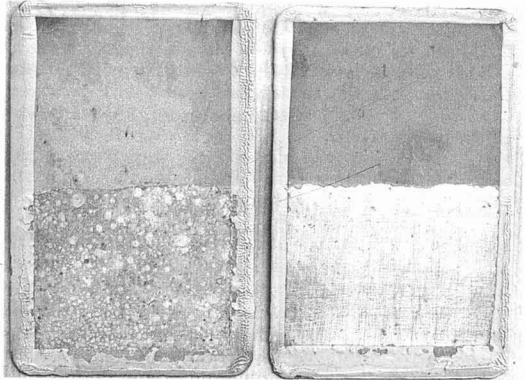


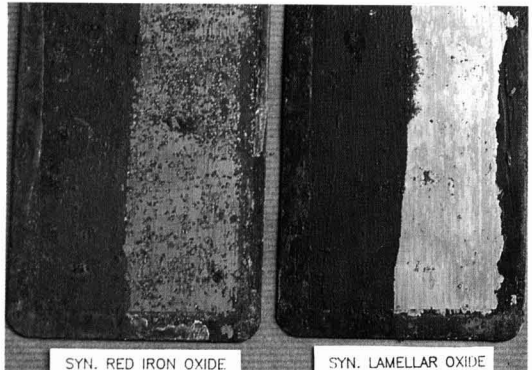
Figure 16

MIO painted girder sections after 17 months exposure at Dungeness "A" Power Station test site. Synthetic MIO was used on upper girder; natural MIO on lower girder. (Courtesy of ITI Anti-Corrosion Limited and CEGB)



Figure 17

Test panels coated with zinc phosphate/iron oxide (3:5) alkyd primers and subjected to BS 3900/F4 cold salt spray test. Coatings were partially removed after 1500 hours to reveal extent of corrosion. See Table 4 for details.



The rate of hydration of zinc phosphate incorporated in a paint film

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Abstract

The rate of hydration of zinc phosphate dihydrate incorporated into an alkyd binder was monitored by X-ray diffraction. The hydration product was the tetrahydrate and the rate was deceleratory throughout the observation period (ca. 400 days). The rate of hydration of a pure sample of dihydrate was of the same order of magnitude suggesting there is little protection offered by the alkyd binder to moisture ingress.

Introduction

Zinc phosphate is a widely used corrosion inhibitor in priming paints¹. It is unusual among pigments in that it is blended as the dihydrate² which contains a stoichiometric quantity of water (8.53% w/w) and water is a well-known corrosion initiator. Some of its limitations have been recently reviewed³. While the mechanism of action is uncertain, it has been suggested⁴ that its purity at the time of blending, and particularly the tetrahydrate/dihydrate ratio, has a pronounced effect on its efficiency. The dihydrate is significantly hygroscopic and will convert to tetrahydrate on storage at high humidity. The rate of conversion of the dihydrate incorporated in a paint film is clearly of interest and will depend on many factors e.g. environmental conditions obtaining at the time of blending and application, the nature of the binder, the substrate preparation, the purity of the starting material etc. This communication describes the results of an experiment in which the rate of hydration of the dihydrate in an alkyd binder was determined using a pure starting material and under carefully-controlled conditions.

Experimental

Zinc phosphate tetrahydrate — this was prepared by the slow addition at room temperature of concentrated phosphoric acid (BDH, AnalaR) to an aqueous slurry of zinc oxide (BDH, Analar) agitated with a Silverson stirrer. The product was filtered at the pump, washed with deionized water until the specific conductivity of the washings decreased to a value of the order of that for laboratory distilled water. The white power was dried in air as a shallow bed at 50°C. The composition of early batches was checked by volumetric analysis for zinc (by EDTA titration) and by gravimetric dehydration to the anhydrate at 550°C; later batches were assayed only by gravimetric dehydration. The composition was always within the range $Zn_3(PO_4)_2(4.00 \pm 0.03)H_2O$.

Zinc phosphate dihydrate — this was prepared by dehydrating tetrahydrate at 110°C for 24 hours. The composition by gravimetric dehydration was $Zn_3(PO_4)_2(2.00 \pm 0.05)H_2O$. The tetrahydrate loses water readily and the dihydrate is quite hygroscopic; all samples were

stored in air-tight containers.

Paint coupons. — The paint had the following composition:

Desmalkyd RS-165 (Bayer)	50g
$Zn_3(PO_4)_2 \cdot 2H_2O$ (sieved to 63 μ)	56.8g
White Spirit	12g
Colorol F	0.5g

A further paint using $Zn_3(PO_4)_2 \cdot 4H_2O$ instead of the dihydrate was also formulated; the composition was similar. The components were blended in an Eiger Mini Motormill with 30cm³ of glass balls as grinding media. The solvent was dried with anhydrous magnesium sulphate and the Colorol F (a wetting and dispersing agent) was added because the tetrahydrate was difficult to disperse in the alkyd. The paints were applied by brush on to a 25 μ thick commercial aluminium foil which had been degreased in an organic solvent. The paint coupons were cured in a slow stream of dry air and stored over silica gel. The film thickness was about 80 μ and two scanning electron micrographs are shown in Figure 1.

X-ray diffraction (XRD). — A Philips PW 1700 automated powder diffractometer was used with copper K_{α} radiation ($\lambda = 1.540598\text{\AA}$) and an accelerating voltage of 45kV. The beam current was 40mA and the beam divergence was 1°. The diffractometer was operated in the step-scanning mode with a counting time of 5s and a stepping increment of $2\theta = 0.01^\circ$; this gives an effective scanning rate of 7° hr⁻¹.

The samples were in the form of circular discs of 34mm diameter and the accumulation time was about 2.8 hours for 2 θ from 5° to 25°. The paint films were scanned at fixed time intervals up to 411 days (see Figure 2); between scans the samples were stored at 20 \pm 2°C in a 93% relative humidity atmosphere.

Results and discussion

The sequential diffractograms are collected in Figure 2. The reflections are fairly broad compared with a powdered crystalline material and this is due to the presence of the alkyd binder and slight preferred orientation of the dihydrate crystallites in the cured film; this is just discernible in Figure 1. The diffractograms exhibit two diagnostic regions:

8° < 2 θ < 12° and 18° < 2 θ < 24°. Comparison of the sequential diffractograms with diffractograms for pure anhydrate, dihydrate and tetrahydrate (Figure 3) shows:

- the initial and early paint film diffractograms only show reflections characteristic of $Zn_3(PO_4)_2 \cdot 2H_2O$ — both the tetrahydrate and the anhydrate show a strong reflection just below 20° and this is absent,
- as the exposure time increases, there is a steady increase in the intensity of reflections characteristic of $Zn_3(PO_4)_2 \cdot 4H_2O$ (2 θ = 9.8, 19.5 and 22.3°) and a steady decrease in the intensity of the dihydrate reflections (2 θ = 11.3°).

Figure 1

Scanning electron micrographs of the fractured edge of the dihydrate paint films. Fig 1b shows the aluminium substrate above the fractured film. In both 1a and 1b some preferred orientation of the crystallites is discernible.

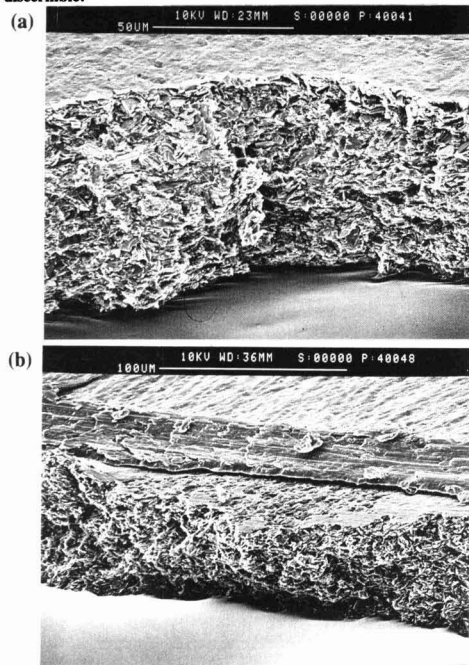
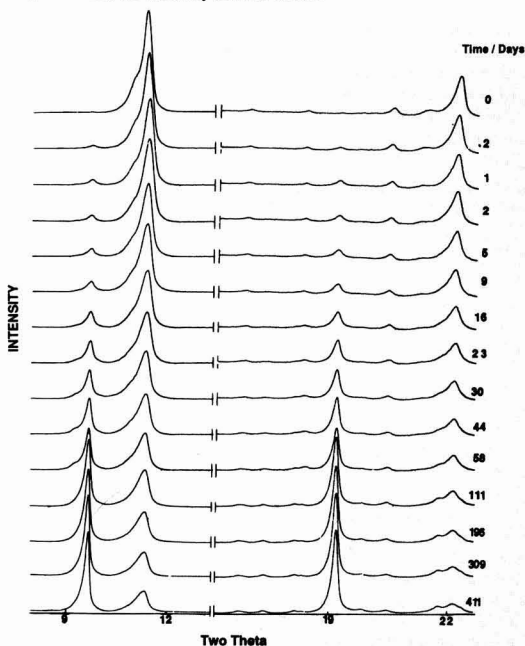
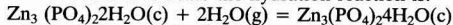


Figure 2

Sequential diffractograms for the dihydrate paint film at different elapsed times; the intensity scale is linear.



These results indicate the hydration reaction is:



The corresponding paint coupons containing a film incorporating $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ were scanned by XRD immediately on receipt, after 7 days and after 314 days. Predictably the diffractograms show constant reflections characteristic of tetrahydrate; the diffractogram for the "as received" sample showed a minor signal at $2\theta = 11.3^\circ$ probably due to dihydrate which formed during storage in a desiccator. This feature had disappeared after seven days exposure.

Using the intensity of the 11.3° reflection in the sequential diffractograms from the dihydrate film as an index for the extent of conversion of the dihydrate to tetrahydrate the rate law for hydration⁵ may be shown to be

$$(1 - [1 - \alpha]^{1/3})^2 = (0.00157 \pm 0.00005)t$$

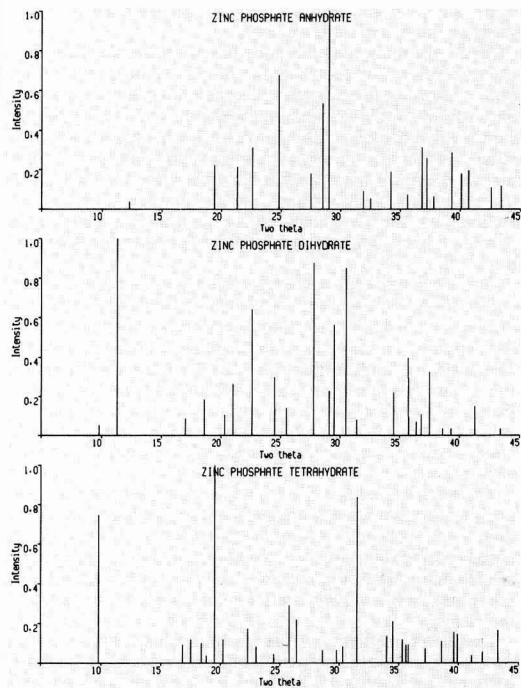
where α is the extent of conversion ($0 < \alpha < 1$) and t is the elapsed time in days. Figure 4 shows a line calculated from this equation and the experimental points up to 60 days, where conversion is $\approx 65\%$. It must be emphasised that the numerical value for the rate constant in the above equation is specific for the particular binder and conditions used in this experiment and consequently, is not of generally applicability. However, the analytical form of the rate law is compatible with a three-dimensional diffusion mechanism for hydration⁵.

In a separate experiment, the rate of hydration of pure zinc phosphate dihydrate was monitored at 20°C in a 93% R.H. atmosphere using a thermogravimetric balance operated isothermally. Readings of mass were taken for 38 hours which corresponds to an extent of conversion of ca. 0.15. The "best

Continued on p.34

Figure 3

X-ray powder diffractograms for pure zinc phosphate, zinc phosphate dihydrate and zinc phosphate tetrahydrate.



Evaluation of anticorrosive paint binders by means of AC techniques: Influence of chemical composition

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Introduction

Anticorrosive protection is highly important, because metallic corrosion reduces the strength of structural steel and this destruction involves direct and indirect losses including problems related to human safety and facts concerning natural resources conservation.

The tendency of a metallic substrate to corrode is a function of the following factors: the surface characteristics of the metal and of the metal/protective film interface, the physical, electrical and electrochemical properties of such film and the nature of the environment in which the system is placed.

The mechanism responsible for the protective action of the organic coatings is highly complex and results from the simultaneous action of different factors.

Taking into account permeability, the organic film plays an important role in the phenomenon of metallic substrate corrosion, since this property is directly connected with the diffusional processes of water, ions and oxygen through the polymeric matrix. And related both with the chemical composition of the latter and with the presence of pores, voids or other defects in the coat.

There are numerous methods based on the application of electric current for analyzing the protective properties of the film¹⁻². Among these methods, accelerated laboratory tests have shown to be useful in predicting the service life of varnishes and paints. They involve both measurements of ionic conductivity in the film using DC techniques³⁻¹² and measurements of impedance in the frequency domain¹³⁻³⁰ and the equivalent resistance at a single frequency³¹ using AC techniques. The latter has also been used for assessing the permeation and the amount of the absorbed water in organic films³¹⁻³⁸.

The measurement of the corrosion potential (E_{corr}) was studied by Wolstenholme³⁹, who established that the displacement of the corrosion potential to higher values is an indication of an increase in the cathodic/anodic areas ratio. This is due to the fact that oxygen and water have penetrated the coating, reaching the metal/membrane interface. Inversely, when the corrosion potential tends to negative values, it indicates that there has been an increase of the anodic/cathodic areas ratio and that the corrosion current is also increasing.

The displacement of the corrosion potential towards more positive values does also suggest that the increasing alkalinity, due to the oxygen reduction reaction, is located in the metal/coating interface, producing delamination. In the case of steel substrates, the measure of more and more negative potentials indicates rust formation, affecting the useful life of the film.

Due to permeability of the coating, which acts as a semi-permeable membrane, the amount of water in it increases with the immersion time⁴⁰ and reaches a steady state when the

osmotic pressure gradient between the two solutions (exterior and interior) is zero.

However, a state of equilibrium may be reached when the mechanical pressure exerted upon the inner solution, caused by the swelling and deformation of the coat, balances the osmotic pressure.

The variation of the mechanical properties of the polymeric matrix (hardness, flexibility, tensile strength, adhesion)³⁴ might serve to explain the influence of film composition upon the behaviour of each interface. Parker⁴¹ stated that plasticizer incorporation modified the mechanical characteristics of the film and an adequate polymeric material/plasticizer ratio is necessary to obtain a highly resistant film.

Polymeric film is constituted by a set of molecular chains, connected by secondary chemical bonds originated in their active centres. Plasticizers must have the ability to neutralize, in a certain extent, those bonds by replacing polymer-polymer bonds by polymer-plasticizer ones⁴²⁻⁴³; thus the degrees of freedom is increased and a more elastic film is obtained.

Plasticizers may be polar or non-polar. The polar character of a plasticizer determines that the plasticization mechanism will be similar to that by which a resin dissolves in a solvent. An additional advantage is introduced: part of the volatile matter in the formulation may be replaced, thus obtaining products with a higher solids content. Consequently, the film deposited on the structure will be thicker⁴⁴.

Non-polar plasticizers reduce the attraction forces among chains through a physical separation of them⁴²⁻⁴³. This type of plasticizer is always used together with polar ones. An example of this is the use of 70% chlorinated paraffin wax (solid), considered a hard resin, used in economic formulations. This inert plasticizer is mixed generally with 42% chlorinated rubber, in order to increase the film mechanical resistance, without modifying substantially its mechanical properties⁴⁵.

The chemical efficiency of a plasticizer depends on the functional groups present in the structure. These groups lead to obtain good compatibility, permanence and stability, and if these properties are not reached, ageing resistance of paint and varnish films is reduced⁴⁶.

The physical efficiency of a plasticizer determines a film with satisfactory adhesion to the metallic substrate. A low solubility of the plasticizer in water represents good humidity resistance and low diffusion tendency⁴⁷.

Some experimental results⁴⁸ show that increasing the amount of plasticizer in the formulation, permeability also increases, and that for the same degree of plasticization, permeability decreases when the molecular weight of the plasticizer increases.

Rudram and Sherwood⁴⁹ determined permeability values for oxygen and water vapour. Depending on these values, the non-pigmented chlorinated rubber films were permeable to

water vapour in the same order as polyurethane and epoxy-polyamide films. They also established that in those films, water vapour and oxygen permeability were lower than in the case of phenolic resin, tung oil or linseed oil varnishes.

Another method to improve physical and mechanical characteristics of a coat is to employ different film forming substances both as compatible resins. This is the case considered in this paper: the authors incorporate chlorinated rubber in different quantities to a phenolic varnish (pure phenolic resin-tung oil) in order to increase sea water resistance⁵⁰.

The purpose of the work was to study the influence of the chemical composition of different varnishes when they are applied on a metallic substrate and immersed in artificial sea water, by using non-destructive laboratory tests. The impedance technique was employed and the corrosion potential was also measured, so as to evaluate the electrical parameters as a function of the immersion time.

Experimental

Preparation of the electrodes

SAE 1020 steel plates 20×8×0.2cm were used as metallic substrate. The percentage composition of the metal, by weight, was: C=0.18; Si=0.02; Mn=0.58; S=0.03; P=0.03; iron being the difference. Surface was sanded to SA 2½ (SIS Standard 05 59 00/1967). The roughness profile of the surface was determined with a Hommel Tester P2-MZ and graphically registered. A Rm=24µm value was established.

These plates were vapour degreased with toluene and coated with the varnish samples whose formulations are shown in Table 1. The films were obtained using a Bird applicator.

The varnished plates were placed in a desiccator for 96 hours to complete drying. Thickness was measured with an

electromagnetic gauge, using an uncoated plate as a reference. The average thickness determined was 55±5µm.

Electrochemical cells

On each panel, and separated by a distance of 1-1.5cm, three cylindrical polyvinyl chloride tubes were placed. The tubes were 10cm long and 5cm diameter and their long edge was flattened. An epoxy adhesive was used to obtain good adhesion to the metal. The geometrical area of each cell was 20cm².

A graphite cylinder with a similar area was used as an auxiliary electrode, while a saturated calomel electrode (SCE) was employed as reference.

Electrolyte

Artificial sea water according to ASTM Standard D/1141-65 was used, without incorporating heavy metals; pH was 8.2.

Electrochemical measurements

For the three cells in each panel and at different immersion times, the corrosion potential measurements were carried out with a Kaise SK-6200 digital multimeter; the impedance module |Z| and the phase angle Φ were determined, at the corrosion potential, at frequencies between 5 and 5×10³Hz, using an impedance vector meter — Hewlett-Packard Model 4800 A.

Data was processed on a P 6060 Olivetti computer, using a set of programmes developed by the authors⁵².

Measurement of the relative dielectric constant

Measurements of the relative dielectric constant were realized for all the varnishes prior and after 30 days immersion in the electrolyte. This was carried out in the form of free films, using a dielectric characteristics meter (dielectric constant and loss factor).

Table 1
Characteristics of the tested varnishes

Membrane identification	Chemical composition (g/100g)	Elaboration process
A	Chlorinated rubber grade 20 52.0	Dissolution of the resin and plasticizer in toluene
	Chlorinated paraffin 42% 22.0	
	Toluene 26.0	
B	Chlorinated rubber grade 20 52.0	Similar to A
	Tricresyl phosphate 22.0	
	Toluene 26.0	
C	Chlorinated rubber grade 20 52.0	Similar to A
	Chlorinated diphenyl 54% 22.0	
	Toluene 26.0	
D	Tung oil 53.3	Copolymerization of tung oil and phenolic resin at 305-310°C
	Pure phenolic resin 26.6	
	Toluene 20.1	
E	Phenolic varnish (80% solids) ... 63.8	Incorporation of a solution of chlorinated rubber and plasticizer to varnish D
	Chlorinated rubber grade 20 17.0	
	Chlorinated paraffin 42% 7.2	
	Toluene 12.0	
F	Phenolic varnish (80% solids) .. 54.6	Similar to E
	Chlorinated rubber grade 20 21.9	
	Chlorinated paraffin 42% 9.4	
	Toluene 14.1	
G	Phenolic varnish (80% solids) ... 38.6	Similar to E
	Chlorinated rubber grade 20 30.9	
	Chlorinated paraffin 42% 13.3	
	Toluene 17.2	

Results

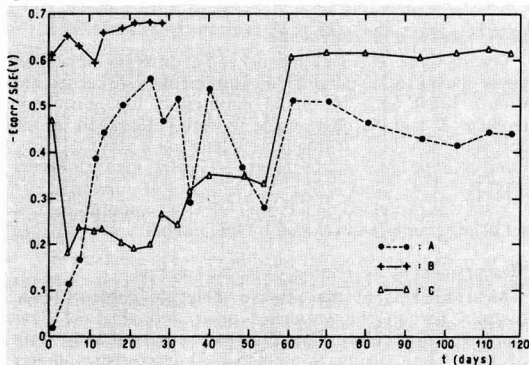
Chlorinated rubber varnishes with different plasticizers (Samples A, B and C).

During the first 60 days immersion, the evaluation of the corrosion potential (Figure 1) shows a different behaviour in each of the tested systems:

a) **System A** (chlorinated rubber-chlorinated paraffin wax) shows an initial value of -0.02V/SCE , which then shifts rapidly and continuously for several hundred millivolts in the negative direction, reaching approximately -0.05V/SCE , and then ranging in these values with growing amplitudes.

Figure 1

Corrosion potential (E_{corr}) vs immersion time (t) in artificial sea water, Varnishes A, B, C, chlorinated rubber with different plasticizers.



b) **System C** (chlorinated rubber-chlorinated biphenyl) starts showing a value of -0.48V/SCE , and later becomes more positive, reaching a peak of -0.18V/SCE , ranges slightly for a certain time and finally grows slowly to the negative side, with intermediate stability periods.

c) **System B** (chlorinated rubber-tricresyl phosphate) suffered a fast corrosive attack; it was tested only for 29 days, period during which the corrosion potential varied between -0.6 and -0.7V/SCE .

After 60 days immersion and up to 118 days, corrosion potential values for systems A and C were practically stable, with variations of a few millivolts.

In order to assess the electrical parameters of the membrane, the ionic resistance (R_m) and the dielectric capacitance (C_m), that serve to define the protective behaviour of the film, both Nyquist's diagram and adjusting algorithms applied to experimental data were used.

Figure 2 summarizes the results obtained for the ionic resistance R_m (Ωcm^2) as a function of the immersion time.

Just from the immersion and until the end of the test (29 days), sample B showed low R_m values (lower than $10^2\Omega\text{cm}^2$); multiple corrosion areas were observed, whose products accumulated in small zones and then dispersed rapidly over the surface, forming an orange coloured layer.

On the other hand, in the case of binders A and C, R_m values remained permanently above $10^6\Omega\text{cm}^2$ for 118 days. It was observed that the metallic surface darkened in some regions below the transparent film; no massive corrosion products or delamination or blistering of the film were established.

Concerning the evaluation of the dielectric capacitance (C_m) of binders A, B and C, as immersion time elapsed (Figure 3), the C_m value for binder B is not only higher but also increases rapidly in a short time, by almost two orders of magnitude.

Figure 2

Logarithm of the ionic resistance (R_m) vs immersion time (t) in artificial sea water, Varnishes A, B and C.

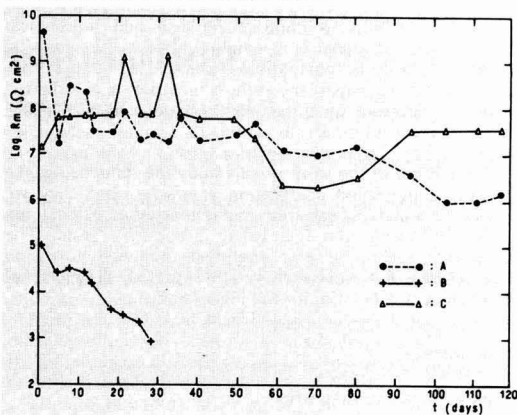
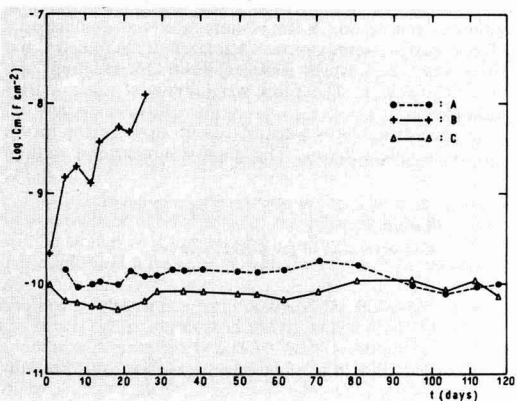


Figure 3

Logarithm of the dielectric capacitance (C_m) vs immersion time (t) in artificial sea water, Varnishes A, B and C.



Samples A and C did not show significant variations of C_m , with values ranging between 7.5×10^{-11} and $1.5 \times 10^{-10}\text{Fcm}^{-2}$ along the whole testing period. Immediately after immersion, sample A showed a very low C_m value ($\sim 1 \times 10^{-14}\text{Fcm}^{-2}$) which is not shown in the graph, and then increased rapidly four orders of magnitude during the first 5 days. Later, it remained within the previously mentioned range.

Chlorinated rubber and phenolic resin binders (Samples D, E, F and G).

Sample G (Figure 4) shows a very unstable corrosion potential (variations between -0.18 and -0.65V/SCE) during the first 50 days. Later it stabilizes in the interval -0.50 to -0.55V/SCE , which is similar to data obtained at the start of the experiment for samples D and F.

The exception is shown with sample E, which showed a considerably stable behaviour during the whole testing period (104 days) and corrosion potential values significantly more positive than those previously mentioned (between -0.18 and 0.06V/SCE).

The R_m and C_m values for these four coatings, as a function of the immersion time, are shown in Figures 5 and 6.

Figure 4

Corrosion potential (E_{corr}) vs immersion time (t) in artificial sea water, varnishes D (phenolic), E, F and G (phenolic with different quantities of chlorinated rubber).

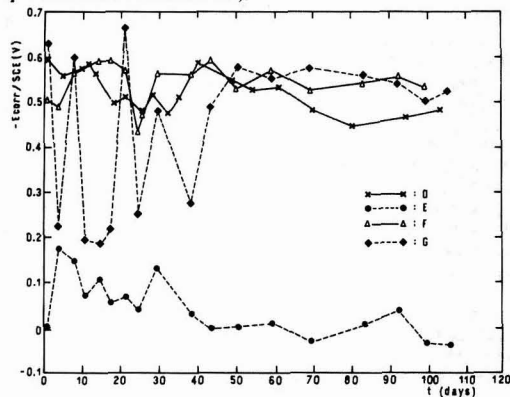


Figure 5

Logarithm of the ionic resistance (R_m) vs immersion time (t) in artificial sea water, varnishes D, E, F and G.

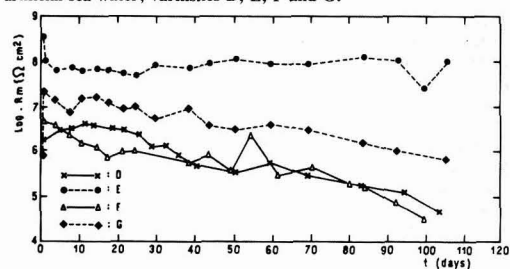
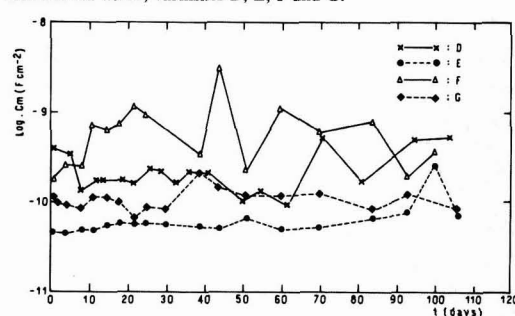


Figure 6

Logarithm of the dielectric capacitance (C_m) vs immersion time (t) in artificial sea water, varnishes D, E, F and G.



The R_m values for samples D, F and G (Figure 5) vary more or less erratically during the first 25 days and then decrease continuously although not uniformly until the end of the test.

The maximum R_m decrease occurred with sample F (from 7×10^6 to $5 \times 10^4 \Omega \text{cm}^2$), while the minimum decrease was detected for sample G, the initial and final values being practically coincident ($\sim 9 \times 10^5 \Omega \text{cm}^2$). However, the latter values increased in more than one order of magnitude during the first days ($R_m \sim 1.5 \times 10^7 \Omega \text{cm}^2$) and decreased slowly.

During the first five testing days, the R_m value of sample E showed a significant decrease (from 5×10^8 to $8 \times 10^7 \Omega \text{cm}^2$); afterwards, it remained practically unchanged.

Figure 6 shows the variation of C_m for the different coatings tested as a function of immersion time.

The values obtained for samples E ($\sim 7 \times 10^{-11} \text{Fcm}^{-2}$) and G ($\sim 1 \times 10^{-10} \text{Fcm}^{-2}$) were practically constant within the limits of experimental error. The latter value is similar to that shown by sample D at 60 days; however, after such a period, C_m became unstable and after some oscillations it increased during the following days.

Finally, the evaluation of sample F also showed oscillations of variable amplitude during the test, although remaining under 10^{-9}Fcm^{-2} , except for the value obtained on the 44th day ($C_m = 6 \times 10^{-9} \text{Fcm}^{-2}$).

Measurement of the relative dielectric constant

The results obtained from the measurements of constant (ϵ) for each one of the coatings tested are shown in Table 2. It may be concluded from these results that, at least in the case of free films, the value ϵ is practically independent from the degree of wetting.

Table 2

Relative dielectric constant

Sample	Dry film	Wet film*
A	2.9 + 0.05 - 0.1	3
B	—	—
C	2.7 + 0.05 - 0.1	2.53
D	2.94 + 0.05 - 0.1	3.1
E	2.76 ± 0.15	2.56
F	2.93 ± 0.15	2.91
G	2.9 + 0.05 - 0.1	3

* After 30 days immersion in artificial sea water

Discussion

The interface may be modified by the metallic substrate, or by a thin film of rust on the metal, or by a thin layer of water⁵³⁻⁵⁵ and finally by the organic film.

The processes taking place in this complex interface are difficult to interpret because after the permeation of water, oxygen and ions, both chemical and adsorption and/or Faradaic electrochemical reactions may occur.

The results obtained from the electrochemical measurements show that, comparatively, there is agreement with the results of E_{corr} , C_m and R_m , as far as their values are shown as a function of immersion time for each one of the binders under test. Thus, the more positive corrosion potential values (smaller areas exposed to corrosion) correspond to the higher values for the resistance to the flow of ions of the electrolyte through the membrane, and with the minimum capacitance values.

In the case of sample B (chlorinated rubber/tricresyl phosphate) high values were found for the initial corrosion potential (-0.6 to -0.7V/SCE) as well as the fast growth of C_m and the decrease of R_m , indicated an accelerated deterioration of the film and consequent large development of corrosion products. The deterioration of the film may be explained by the fact that tricresyl phosphate is a highly hydrolyzable substance due to its high polarity. As result of this, the film became very permeable to water, oxygen and ions, increasing the conductivity of the interface solution and facilitating the cathodic reaction of oxygen ionization,

complementary of the metallic dissolution process.

It is well-known that the fundamental cathodic reaction in the electrolyte medium used for these experiences, is the reduction of oxygen to hydroxyl ions. The pH of the metal/organic film interface became highly alkaline with subsequent degradation of saponifiable films.

During the first days of immersion, binders C (Figure 1), D, F and G (Figure 4) show a fast change of the corrosion potential towards the positive side. This indicates that there is a growth of the cathodic/anodic areas ratio, as a result of water and oxygen diffusion to the metallic surface. Inversely, samples A (Figure 1) and E (Figure 4) show a displacement to more negative values, indicating a progressive increase of the already existing anodic areas or the formation of new ones. Further oscillations of the corrosion potential to 50-60 days, whose amplitude depends on the number and size of the metal area submitted to corrosion and of the corrosion process rate, may be explained on the basis of the formation, growth and blockage of the defects⁵⁶ in the less protected areas by the organic coating. After 50-60 days and until the end of the tests, the stability of the corrosion potential values shows that no new corrosion areas appear on the rest of the surface coated with the organic film. These results were confirmed by visual inspection of the samples.

As a general rule, a good correlation was obtained between the changes in the electrical properties of the coated steel and the deterioration of the organic film producing the metal corrosion.

The Rm variation as a function of the immersion time agrees with the assumption that there is a connection between this parameter and the porosity of the protective coating⁵⁷⁻⁵⁸. For short immersion periods, the failure areas are usually small and therefore, Rm is large and remains practically constant unless changes occur due to the rapid absorption of water and ions by the film. During further stages and depending on the kinetics of the corrosion processes in the metal/coating interface, a decrease of Rm may be detected, its rate depending on the deterioration of the polymer due to its interaction with hydroxyl ions.

The samples plasticized with chlorinated paraffin (A) and chlorinated diphenyl (C) showed a good protective behaviour along the whole test, with Rm values ranging between 10^6 and $10^7 \Omega \text{cm}^2$ (Figure 2) and of $C_m = 10^{-10} \text{ Fcm}^{-2}$ (Figure 3). These values were attributed to the high chemical resistance of the membranes, caused by their low polarity. The latter property is the direct cause of the water cluster formations^{59,60}, which are typical in hydrophobic coatings such as those under examination (A and C). The higher C_m values and lower Rm values in sample A, as compared with those for sample C, are in accordance with studies reported by other authors⁴⁸, indicating that for the same plasticization value, water permeability decreases as the molecular weight of the plasticizer increases. After 80 days, the Rm values of sample A showed a transitory decrease and a further stabilization. It has been shown that there is a plasticizer loss (dissolution) for this type of formulation, thus increasing the number of "holes" in the polymeric matrix and favouring the above mentioned cycle: electrolyte permeation-corrosion process-blocking by the action of the corrosion products formed.

At the end of the electrochemical tests, a visual inspection of sample A showed the presence of corrosion in five small and well defined areas, although there was no loss of adhesion of the coating. On the other hand, no corrosion signs were found in sample C.

The behaviour of sample D (oleoresinous varnish) showed a slight initial increase in Rm (Figure 5) and a further continuous decrease after 12 days immersion. Transitorily, after 55 days, a significant Rm increase was observed, due to the accumulation of corrosion products in the only area attacked. Later Rm decreases rapidly and follows regularly

with this tendency. The reduced protective property may be attributed to the fact that the increase in pH of the metal/film interface (through oxygen ionization) produces the saponification of the varnish coating (formation of soluble soaps), contributing to the degradation of the film in contact with the cathodic areas, the increase of the anodic areas and decrease of Rm. Eventually, this phenomenon may occur inversely, when the rate of the thickening of the corrosion products layer is greater than the delamination rate of the coating.

The chlorinated rubber/phenolic varnish systems tested along 104 days, sample E showed a constant and high barrier effect ($R_m \approx 10^7 \Omega \text{cm}^2$). This feature is attributed to the incorporation of chlorinated rubber to the oleoresinous formulation, which reduces water permeability and increases resistance to chemicals, with no corrosion products formation and with very good adhesion.

A slightly abnormal behaviour (lower Rm values than sample E) was obtained in the case of samples F (21.9% chlorinated rubber) and G (30.9% chlorinated rubber), associated with structural defects in the film a few areas of attack were observed but there was no delamination of the coating. These results were confirmed in subsequent tests employing systems with thicker films⁶¹.

The interpretation of capacitance/time curves, according to Wormwell and Brasher⁵⁷ is at first sight more complex. The initial increase in capacitance is certainly connected with water absorption by the varnish coating; whether the uptake of salt exerts a direct effect is not certain. These authors gave an explanation for the higher differential capacitance value in the electrical double layer of the bare steel/sea water interface ($C_{dl} = 20 \times 10^{-6} \text{ Fcm}^{-2}$) as compared to that of an organic coating ($C_m = 10^{-12}$ to 10^{-9} Fcm^{-2}). They assumed that the capacitance per unit area at the steel/sea water interface is controlled by the thickness of the electrical double layer and of any thin film of oxide or other reaction product. Since the thickness is very small (ca. 10^{-8} cm for the double layer and up to 10^{-6} cm for air formed oxide films), the capacitance may reach very large values for quite small areas. This high capacitance, in parallel with the low capacitance due to the varnish coatings, gives a high measured capacitance C_T , which is defined as: $1/C_T = C_{dl} + C_m$. Any such film underneath the varnish, being in series with the varnish, does not appreciably affect the measured capacitance C_T , defined in this case as: $C_T = 1/C_{dl} + 1/C_m$.

When the capacitance/time plots show a meaningful decrease after several days, the most probably explanation is that for a given area of varnish failure the capacitance is decreased by an increase in thickness of the rust film

Sometimes, any effect of rust in reducing capacitance at areas of early failure is more than offset by an increase in capacitance with an increase in area. Nevertheless it is possible, in the case of an organic coating, breaking down extremely slowly, due to the thickening of the rust deposit to mask completely the capacitance rise caused by the slowly increasing area.

The validity of this interpretation for the changes in the capacitance values could be fully confirmed by considering the permittivity measurements performed in the laboratory for all the tested samples. As it may be seen in Table 2, no significant changes have been detected in the results obtained with dry and wet films; therefore the variations in the C_m values for some films shown in Figure 3 and 6 must not be attributed to modifications in the dielectric constant of the membrane.

Consequently, factors such as adhesion, chemical resistance and water and delamination resistance of the membrane in every formulation must be considered as exerting a direct influence upon the ratio between thickness of the rust layer and the growth of the bare metallic area.

From this viewpoint, samples A and C (Figure 3) justify their stability and low capacitance on the basis of the hydrophobic characteristics of the chlorinated rubber/plasticizers systems under analysis. In contrast, the rapid breakdown of varnish B in the first days of immersion, due to tricresyl phosphate dissolution, is showed by a quick rise in its capacitance values.

In Figure 6, the comparison of the results obtained serves to corroborate, specially as immersion time increases, the above mentioned influence of the chlorinated rubber addition upon the phenolic varnish properties. Thus, except for sample F until 90 days, the C_m values for the other two chlorinated rubber/phenolic varnish mixtures (E and G) were below those corresponding to sample D (phenolic varnish alone). This implies a lower degree of deterioration and therefore a longer useful life of the coating.

Conclusions

It was established that there was a good correlation between the values of the electrical properties ionic resistance (R_m) and dielectric capacitance (C_m) of the organic films tested and the corrosion potential (E_{corr}) of the metallic substrate.

At a given plasticizing degree, the sample containing chlorinated diphenyl showed to be more efficient than that formulated with chlorinated paraffin, due to its lower water absorption and solubilization. The use of tricresyl phosphate in chlorinated rubber binders in continuous contact with an electrolyte as sea water is not convenient and the coat obtained is highly hydrophilic.

The protective properties of the coatings under test is directly related to its chemical inertia.

The measurements of the dielectric constant performed in each coat, in the form of humidified or dry free film, showed that the value of this parameter is independent of the water content in the membrane. The authors considered that it is possible to extrapolate this conclusion to the case of supported films, in spite of the modifications to their physical properties introduced by metal-film interactions.

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Continued on p.30

Underfilm corrosion of steel induced by saline contaminants at the metal/paint interface

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Abstract

Residual surface contaminants mainly sulphates and chlorides, resulting from the exposure of steel to industrial and marine atmospheres, before painting, can significantly influence the behaviour and lifetime of paint coatings.

This research studies the corrosion of steel beneath a thin varnish film when variable amounts of FeSO_4 and NaCl are present at the steel/varnish interface. The effects produced by both contaminants when acting separately and in combination are analysed. In the first case underfilm corrosion of steel depends on the surface concentration of contaminant. In the joint action of both contaminants a quasi-additive effect is observed.

Introduction

The atmospheric contamination exerts a strong influence on the durability of anticorrosive paint coatings, thus giving rise to: (i) the atmospheric corrosion of the metal substratum which subsequently receives the organic coating; (ii) the degradation of the film properties during its application and curing and (iii) the progressive deterioration of the steel/paint system as a result of its exposure to the atmospheric agents. This study deals with the first of the aforementioned effects.

The subject is of considerable practical interest, taking into account the frequency with which paint coatings are applied to steel that has been previously exposed to polluted atmospheres.

The exposure of steel to industrial and/or marine atmospheres leads to the formation of hydrosoluble products, such as ferrous sulphate and/or chlorides, among the corrosion products. Even when, in the best situation, a deep cleaning of the metallic surface is carried out by means of efficient techniques of abrasive blasting, the presence of a certain amount of those hydrosoluble contaminants is inevitable¹. Due to the electrochemical corrosion process, the SO_4^{2-} and Cl^- ions locate at the bottom of the corrosion pits, among the surface folds, etc., which hinders their complete elimination².

The presence of hydrosoluble species at the steel/paint interface promotes osmotic blisters of the paint film in humid environments. Furthermore, FeSO_4 and NaCl are substances which actively stimulate corrosion of steel. Both processes, osmotic blistering and underfilm rusting cancel out in very short periods of time the protective properties of paint coatings applied to steel.

In a previous research project the presence of FeSO_4 and NaCl at the steel/paint interface and its effect on the deterioration of paint systems was studied^{1,3}. It was found that concentrations of 100-500mg/m² of NaCl , or 1000-2500mg/m² of FeSO_4 , could be enough to cause premature deterioration of the paint coating. The underfilm corrosion of steel was not quantified in the aforementioned research. In contrast, the present study⁴ analysis not only the deterioration of the coating, but also the corrosion of the steel underneath a thin varnish film.

Also of interest is to ascertain the effect produced by both contaminants acting jointly, since this circumstance occurs often in practice (e.g. industrial zones near the coast). No study dealing with this aspect was found in the literature.

Experimental

The specimens, 5 × 5 cm, were prepared from a flat mild steel plate 0.5 mm thick. Then they were completely degreased with trichlorethylene. Subsequently, on one side of the specimen different concentrations of contaminants FeSO_4 and NaCl were applied (Table 1), as well as combinations thereof.

The application of the contaminant was carried out by pouring the corresponding dose of the contaminating solution onto the centre of the specimen by means of a pipette. Afterwards a glass rod was used to spread the applied solution over the entire test surface, leaving a liquid coat as uniform as possible. The contaminant solutions consisted of water-methanol mixtures in which the required amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and NaCl had been dissolved, depending on the desired level of contamination (Table 1). In order to avoid as much as possible the formation of rust in the time interval between the application of the contaminant solution and the application of the varnish coating, a minimum amount of distilled water was used to dissolve the corresponding quantities of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and NaCl . The total volume of the contaminating solution was reached by filling the remainder with methanol. Once the contaminating solutions were applied to the steel surfaces, these were placed in a stove where the temperature was 80°C, thus bringing on a fast evaporation of the solvents.

Subsequently, by means of a wire-wound rod a peelable (strippable) varnish film was applied to a dry film thickness of 8 μm. The use of a peelable coating enabled the observation of the corrosion products formed at the steel/varnish interface, as well as facilitated their collection for subsequent identification. The coated specimens were left for a week in the laboratory at room temperature for complete curing. Their edges were then protected by dipping them in a melted mixture of wax and paraffin.

The specimens were subsequently placed in a chamber where they were subjected to an aerosol of distilled water. The temperature inside the chamber was kept constant at 32°C. Several series of specimens were prepared and removed from the chamber after different time intervals: 26, 85 and 485 hours.

Results

Deterioration of the varnish film

The permeation of aggressive species through the varnish film to interact with the base steel depends upon the condition of the organic coating. When the coating is in perfect condition, oxygen, water, ions, etc., have to pass through the coating film by diffusion processes. In contrast, when the coating is seriously deteriorated, perforated, etc. a massive transfer of aggressive species is made possible via defects in the varnish films. Thus, it was of interest to know the type of film deterioration induced by the presence of saline contaminants at the steel/paint interface.

Coating deterioration during the humidity test was in form of blistering. The blistering morphology changed in function with the type of contaminant and its concentration at the interface. When the contaminant was FeSO_4 , a fine and dense

blistering appeared on the coating surface, the size of the blisters increasing slightly with the exposure time. However, when the contaminant was NaCl the number of blisters was less and their diameter greater. This difference was found to be more pronounced as the NaCl concentration at the interface was increased.

In regard to the joint action of both contaminants, it was noted that the blistering morphology depended on the relative concentration of each of the contaminants in the mixture. The mixtures containing the highest NaCl concentration (500mg/m²) and a low concentration of FeSO₄ promoted the typical blistering produced by chlorides: few but large blisters. The remaining combinations produced the typical blistering induced by sulphates: numerous small blisters.

Due to the high elasticity of the varnish film the blisters were able to withstand bursting for a long period of time, thus allowing the accumulation of water (which was forced to permeate through the coating by osmosis) and corrosion products inside them. When the pressure exerted by such products exceeded the elasticity limit of the varnish film, it perforated permitting the exit of corrosion products. This situation occurred only at high concentrations of contaminants at the interface, and after prolonged test periods.

Underfilm corrosion

One series of specimens was employed to follow the evolution of corrosion of steel under the coating. This was carried out by weighing the steel before the application of the contaminant solution and then again after the test, once the varnish film and corrosion products had been removed. The coating was peeled off and the corrosion products eliminated by an inhibited solution of hydrochloric acid. The weights were taken with an analytical balance of 0.1mg precision. The greater the attack on the underlying steel, the more difficult it was to remove the varnish coating.

Table 2 shows the underfilm corrosion of the steel after 26,

185 and 485 hours of exposure to the humidity chamber. When contaminants were not applied to the steel, rust at the interface was not observed, even after 485 hours of testing. However, the presence of interfacial contamination, even at the lowest concentration, promotes a measurable corrosion of the steel after only a few hours of testing.

Morphology and composition of corrosion products

Very little precise information exists in the bibliography about the composition of the rust that forms under the paint coating when they are exposed to atmospheric agents. To obtain such information a series of specimens was designated for investigating the nature of the corrosion products formed beneath the varnish film. The identification of corrosion products was carried out with the help of Mössbauer Spectroscopy.

The spectra were obtained at ambient temperature in a conventional, constant-acceleration spectrometer equipped with a Co-57 source in a matrix of Pd. The technique employed was either transmission or reflection according to the thickness and the conductivity of the corrosion products films. The transmission modality was employed in those samples in which it was not possible to peel off varnish film from the metallic support due to the advanced deterioration of the coating. This technique was also utilized in those samples where, even though the varnish could be detached, the conductivity of the substratum was very low. In this case the spectrum was made with the detached film of varnish which carried a large amount of corrosion products adhered to their surface. Once the experimental spectra were obtained adjustments were made to standard Lorentzian curves.

At short exposure times (26 hours), the main corrosion product was γ -FeOOH (lepidocrocite) of a reddish-brown colouring. Longer test periods (185 hours) show, along with γ -FeOOH, other varieties of oxyhydroxides: α -FeOOH (goethite) when the contaminant was FeSO₄, and β -FeOOH (akagenite) in the case of interfacial contamination by NaCl. At extended test periods (485 hours) the presence of Fe₃O₄

Table 1
Contaminating solutions and dosage used for different interfacial contamination levels.

Contaminant: FeSO ₄				
Contamination level, mg/m ²		Contaminating solution		Dosage (cm ³) for a surface area of 25cm ²
Expressed as SO ₄ ²⁻	Expressed as FeSO ₄	Total volume (cm ³)	FeSO ₄ · 7 H ₂ O dissolved (mg)	
50	79	125	452	0.1
100	158	125	904	0.1
250	395	125	2260	0.1
500	790	125	4520	0.1
1000	1580	250	4520	0.4

Contaminant: NaCl				
Contamination level, mg/m ²		Contaminating solution		Dosage (cm ³) for a surface area of 25 cm ²
Expressed as SO ₄ ²⁻	Expressed as FeSO ₄	Total volume (cm ³)	NaCl dissolved (mg)	
5	8	125	26	0.1
10	16	125	51	0.1
20	33	125	103	0.1
50	83	125	258	0.1
100	165	125	516	0.1
500	825	125	2576	0.1

(magnetite) was detected, in greater proportion as the underfilm corrosion of steel was higher. The corrosion products acquired darker colours.

In view of these results, it may be pointed out that the corrosion products formed under the varnish coating are similar to those found on the uncoated steel exposed to the atmosphere⁵.

Impedance measurements

A series of specimens was designated for electrochemical impedance measurements. This was intended to quantify and follow the protective capability of the coating, as well as to know whether an estimation of the underfilm corrosion of the steel could be made from the impedance diagrams.

Once removed from the humidity chamber, the painted specimens were subjected to a sweep of frequencies by which the spectrum of impedance was obtained.

The experimental dispositive used is shown in Figure 1. The measuring cell was composed of three electrodes: the steel subjacent to the coating which acted as working electrode (WE); a 15cm² platinized titanium sheet which acted as counter-electrode (CE); and calomel saturated electrode as the reference (RE). Distilled water was used as electrolyte. The impedance measurements were taken one hour after the distilled water had made contact with the varnish coating.

The impedance measurements were made using a Solartron 1170 frequency response analyzer connected to a Solartron 1186 potentiostat. The amplitude of the signal applied was 10mV, and the frequency ranged from 55kHz to a few mHz.

At short exposure times to the humidity chamber and with low concentration of contaminant at the steel/varnish interphase, the Nyquist diagram acquired the shape of straight lines very close to the imaginary axis. As the contaminant concentration was increased and the exposure time lengthened, the impedance diagram resulted in an arc of circumference at high frequencies, and a more or less curved tail at low frequencies (Figure 2).

In the case of impedance diagrams in the form of a straight line running parallel to the imaginary axis, the varnish film capacitance is the only parameter that can be calculated. This was made by means of the expression:

$$C_p = \frac{1}{Z'' \cdot \omega}, \text{ for } \omega \rightarrow \infty$$

where ω is the angular frequency and Z'' the imaginary part of the impedance vector.

When a semicircle appears in the high frequency range of the impedance diagram, the ionic resistance of the varnish coating, R_i , can be also calculated. This was made by measuring the diameter of such semicircle. Nevertheless, the calculation of the charge transfer resistance (and thus the corrosion rate of subjacent steel) was not feasible, as the low frequency semicircle was not defined⁶. Figure 2 illustrates the R_i and C_p values corresponding to each diagram.

It is common to relate Nyquist plots in the shape of straight lines running close to the imaginary axis with coatings in perfect condition. In this case it should be anticipated a practically total absence of corrosion in the metallic substratum. The results of this study demonstrate the imprecision of such consideration. For example, for an interfacial chloride contamination of 50mg/m², after 485 hours of exposure to the humidity chamber, the coating becomes totally blistered, with

Figure 1
Schematic representation of the experimental dispositive used for impedance measurements.

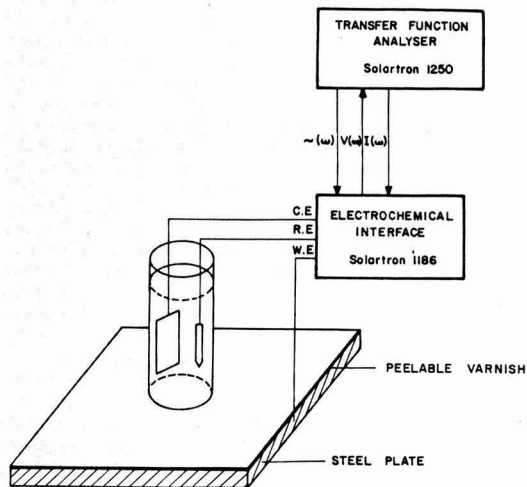


Table 2

Underfilm corrosion of steel (mg/dm²) in both contaminated and uncontaminated samples coated with a varnish film of 8µm thickness. After 26 hours (A), 185 hours (B) and 485 hours (C) of exposure in a humidity condensation chamber.

Contamination by Cl ⁻ , mg/m ²	Contamination by SO ₄ ²⁻ , mg/m ²																	
	0			50			100			250			500			1000		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
0	N.D.	N.D.	N.D.	42	108	147	70	151	228	57	167	323	134	307	405	105	456	545
5	14	47	80	50	144	209	68	204	320	81	253	331	100	298	390	118	420	472
10	23	56	91	49	122	235	66	109	209	48	263	392	104	297	416	105	394	517
20	29	110	137	56	121	271	69	211	331	81	276	459	108	270	417	89	484	603
50	27	107	208	48	142	259	71	208	288	80	331	408	88	287	465	111	370	695
100	32	208	291	51	180	310	82	253	357	83	348	511	114	320	473	135	438	528
500	70	203	366	104	307	526	94	353	453	125	348	538	179	413	600	205	510	633

N.D. Underfilm corrosion of the steel is not observed, nor is it detected with the gravimetric technique employed.

small blisters distributed all over the surface, and the underfilm corrosion of steel reached the value of $208\text{mg}/\text{dm}^2$ (Table 2). However, the corresponding impedance measurements indicate a practically capacitive behaviour (Figure 2).

The varnish coating used shows low capacitance values even after prolonged exposure times, which barely increase as the saline contamination is increased in the interface. On the contrary, ionic resistance is significantly diminished with the saline level. The apparent contradiction between high underfilm corrosion (and significant film blistering) and the capacitive behaviour of the system may be explained as due to the great elasticity of the coating. On account of this, important accumulations of corrosion products inside the blisters and at the steel/varnish interface are possible without the coating being cracked or perforated.

Discussion

The iron dissolution in neutral media underneath paint films must depend on the possibilities for water and oxygen to reach the metallic surface, so the cathodic reaction of oxygen reduction can be verified.

Free films of the varnish used in this research showed permeation rates for water vapour and oxygen (under aqueous film) of 1.2×10^{-2} and $0.85 \times 10^{-3} \text{g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ respectively^{7,8}. Taking into account that for the dissolution of one gram of iron, to form FeOOH , similar amounts of oxygen (0.43g) and water (0.48g) are needed, it is reasonable to think that the permeation rate of oxygen — ten times lower — be the controlling step of the corrosion process under the varnish film.

On this assumption and according to the above mentioned value of oxygen permeation rate one would expect an underfilm corrosion of $197.6\text{mg}/\text{dm}^2 \cdot \text{day}$ after 485 hours of exposure in the humidity condensation chamber. This figure

contrast markedly with the absence of corrosion (at least not measurable with the gravimetric technique employed) for uncontaminated interfaces (Table 2).

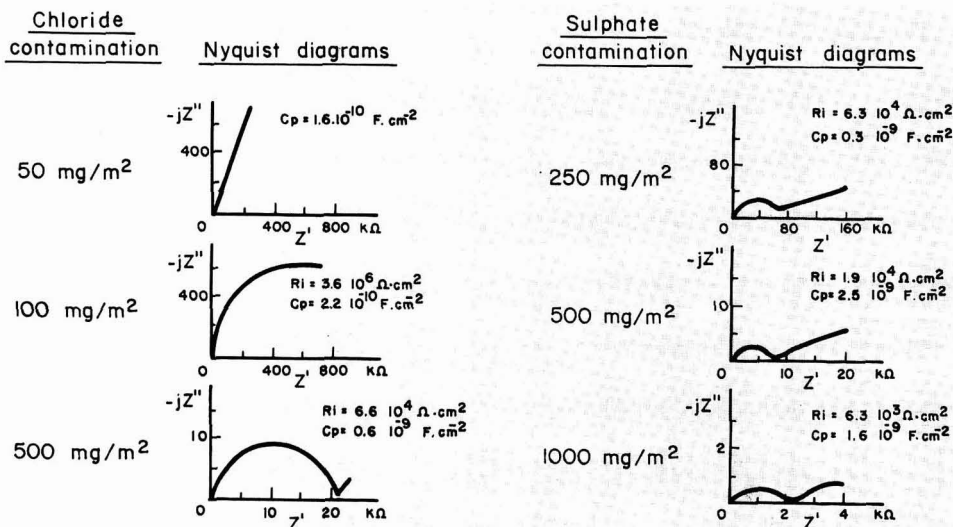
Therefore, it may be concluded that the controlling factor for the underfilm corrosion process on uncontaminated surfaces is not the arrival of oxygen to the steel/varnish interface. The fact that corrosion significantly increases with interfacial surface contamination (Table 2) suggests that the ionic conduction resulting from the saline deposit in the interface, is the real controlling factor. Actually, low concentrations of contaminant at the steel/varnish interface suffice for promoting a significant corrosion of the subjacent steel after very few hours of testing (Table 2).

In the case of highly contaminated surfaces, the ionic conduction is no longer controlling the under film corrosion, which is now governed by the diffusion of oxygen through the varnish film. The following conjectures support this idea: (a) the above mentioned lesser permeation rate for oxygen, and mainly because of the entrance of water by osmotic processes through the varnish film caused by the existence of soluble substances at the steel/varnish interface, and (b) the agreement between the consumption of oxygen derived from underfilm corrosion data (when the varnish film is still in good condition) and transport of oxygen through free films of varnish. For example, underfilm corrosion data of steel after 26 hours of exposure in the humidity condensation chamber were $0.70 \times 10^{-3} \text{g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ and $1.34 \times 10^{-3} \text{g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ for an interfacial contamination of $500\text{mg}/\text{m}^2$ of NaCl and FeSO_4 , respectively (Table 2). From these values the estimated consumption of oxygen is 0.28×10^{-3} and $0.53 \times 10^{-3} \text{g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ respectively, figures in consonance with the permeation rate of oxygen ($0.85 \times 10^{-3} \text{g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$) through the varnish film.

The accumulation of water at the steel/varnish interface as a result of the osmotic process, and of rust from the corrosion cyclic process^{1,3} promotes blistering of the coating once the pressure that both products exert exceeds the adhesion strength of the varnish film to the metallic support.

Figure 2

Impedance diagrams (Nyquist) for the steel/varnish system with different levels of contamination at the interface. Time of exposure in the humidity condensation chamber: 485 hours.



Effect of contaminant concentration

In relation to both processes, osmotic blistering and underfilm corrosion induced by the presence of hydrosoluble contaminants at the steel/varnish interface, the question arises: Is there a critical threshold of contaminant concentration which causes both processes? The experimental results do not suggest the existence of such critical levels, in contrast to what occurred in a previous work^{1,3} where commercial paint systems were employed. At low concentrations of interfacial contamination by NaCl (5mg Cl⁻/m²) blistering of the varnish film and measurable underfilm corrosion have been detected, whereas in the previous work^{1,3} blistering did not take place until chloride concentrations of 60-300mg/m² were reached. The same occurred for an interfacial contamination by FeSO₄. These differences may be attributed to the low film thickness considered in this study, the low adherence of the peelable varnish, and the absence of corrosion-inhibiting pigments

which could totally or partially deactivate the saline contaminant by forming insoluble compounds⁹. Further research will enable us to understand more fully the role played by these factors.

Both the blistering of the varnish coating and the underfilm corrosion of steel increase as does the surface concentration of contaminant (Table 2), although the corrosion rate of steel lessens with time (Figure 3).

Effect of the joint action of both contaminants

Figure 4 illustrates, in a tridimensional diagram, the combined effect of the contaminants (sulphates and chlorides) on the corrosion of steel under the varnish film, after 485 hours of exposure in the humidity condensation chamber. For a determined level of one of the contaminants, the incorporation of the second contaminant promotes an increase in the corrosion of the underlying steel.

One must consider questions such as: Does there exist an

Continued on p.30

Figure 3

Evolution of underfilm corrosion of steel with exposure time at different interfacial contaminations. A, 20mg Cl⁻/m²; B, 100mg Cl⁻/m²; and C, 500mg SO₄²⁻/m².

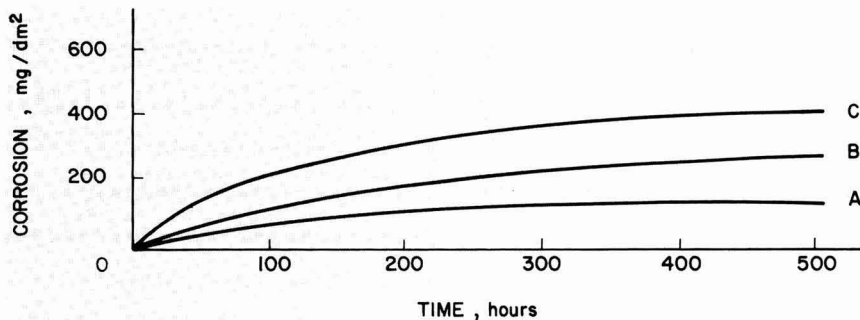
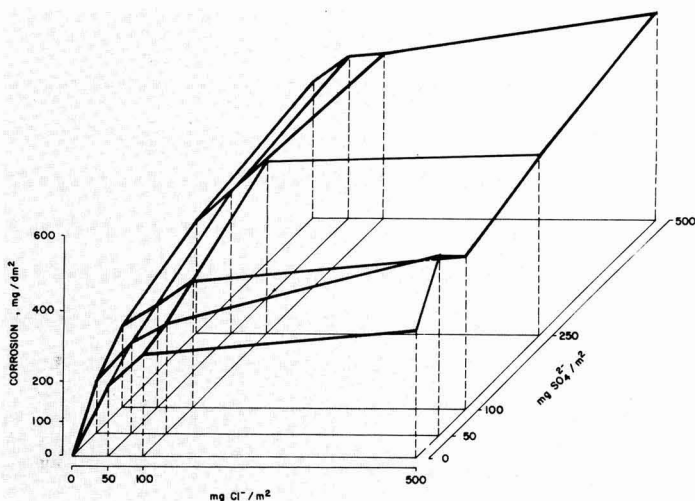


Figure 4

Tridimensional diagram showing the influence of the contaminants FeSO₄ and NaCl, and combinations thereof, on the underfilm corrosion of steel.



Tainting – an analyst's approach

D. L. Easterby, Coates Lorilleux Ltd, Cray Avenue, St Mary Cray, Orpington, Kent BR5 3PP, UK

Food packaging has three important functions to serve. It must convey information concerning the product, it must attract the attention of the potential purchaser and it must protect the goods from premature spoilage. In terms of the total cost of the item, the packaging represents only a relatively small part; and in turn, the ink used represents very much less. The inkmaker therefore takes every precaution to ensure that the inks supplied are suitable for the purpose intended and will not lead to expensive rejection of the package.

This article will look at a case where a combination of factors, beyond the control of the inkmaker, led to food contamination and severe tainting of the product. It will follow the investigations of the Coates' Inks Division Analytical Department in establishing the source of the taint and identifying the nature of the contaminant.

Background

The taint was present in the top pastry crust of a fruit pie product distributed by a well known chain of supermarkets. It was not discovered until a quantity of pies had been returned by the public.

A substantial claim for damages ensued which was passed from retailer to baker, from baker to printer and from printer back to Coates, the original ink manufacturer.

Samples of tainted and untainted pies, 'good' and 'bad' prints plus unprinted board were supplied for analysis.

The analysis

Prior to any physical or chemical investigations of the samples, a complete historical background to the problem was established. This highlighted several very important pieces of information which were used as the basis for the ensuing analytical studies:

- the taint was present in the top pie crust only
- the taint developed on storage
- the problem was isolated to one print run
- the print run used one complete batch of board
- other prints of the same job were produced before, after and alongside the 'complaint' job and subsequently caused no taint problem.

An initial examination of these facts indicated that the inks were the least likely cause of the taint. The initial work, therefore, concentrated on investigating the tainted pies, the print samples and associated board samples.

Conventional solvent extraction and headspace techniques coupled with capillary gas chromatography were used to examine tainted and untainted pastry, 'good', 'bad' and unprinted board. These sensitive sampling methods showed no significant difference between any of the samples.

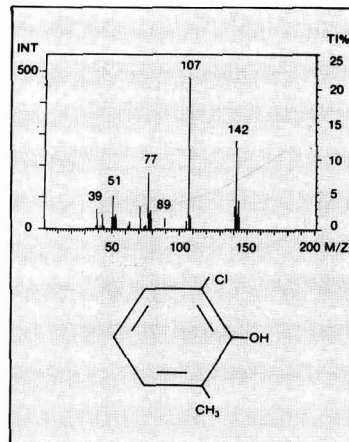
A two phase distillation/extraction/concentration technique, developed by Likens & Nickerson¹, was applied to the 'good', 'bad' and unprinted material. This identified an extract from the 'bad' prints which had a distinct chemical odour and which imparted the same taint to standard pastry as that experienced in the tainted pies. One particular batch of board produced the same tainting extract. The taint was described as 'antiseptic'.

Armed with this information, samples of tainted pies, 'bad' prints and the extracts were submitted to the Food Research Association at Leatherhead who have extensive experience of this type of problem. The samples were first subjected to the

FRA's own taint tests and the indications were that chlorinated phenolics were likely to be present. Gas chromatography/mass spectroscopy, a technique that at that time was not available within the Coates Group, was then used to examine the various extracts supplied to establish if they contained chlorinated compounds.

The GC/MS had to be operated in its most sensitive mode, Selected Ion Monitoring, because of the very low taint threshold of these compounds. A chlorinated cresol, 6-chloro ortho cresol (Figure 1) with a taint threshold of >0.5 ppb (equivalent to 1 teaspoon full in 50,000 tonnes), was shown to be present in both 'tainting' and unprinted board. One sample of unprinted board in fact contained 200ppb of this compound.

Figure 1
GC/MS spectrum and structure of 6-chloro ortho cresol



The source of the contaminant had been conclusively established – it was from the board and not the inks.

The contaminant

The next stage of the investigation was to examine how this contaminant had got into the board.

A literature survey revealed several instances of this type of contaminant causing taints in foodstuffs over the past 30 years. In some instances, the chlorinated phenols had been formed in situ from the reaction of common bleaches with residual phenolic compounds in packaging materials and even flooring.

A complete check of the printer's warehousing facility showed that the board could not have been contaminated in these areas. Therefore the board must have been contaminated when it left the papermill. How could this have happened?

It is possible that this compound could have formed in situ during bleaching of the wood pulp or treatment of the water supply in the papermill. Compounds of this type are readily

formed by the action of chlorine on cresols but, if this were the case, another isomer, 4-chloro ortho cresol, would be predominant. This isomer was shown to be absent from the contaminated board. In any event, the tainting effect of 6-chloro ortho cresol is so well known that, if it is formed as a by-product in a chemical plant in the UK, it is automatically isolated and immediately incinerated.

The 6-chloro ortho cresol must therefore have been unwittingly introduced into one of the raw materials used in the board manufacture. Wood pulp was the most likely candidate. Further work by Coates in conjunction with the board manufacturer established that a higher concentration of 6-chloro ortho cresol was present in one of the layers of the board. As each layer is produced from a different pulp, this indicated that a particular pulp had been contaminated. The origin of the pulp is believed to have been one of the underdeveloped countries where there is less control of chemicals such as these and they may find use as fungicides or slime control agents.

Conclusion

This investigation is typical of the type of work carried out by Coates' Analytical Department. The work identified the minute quantity of contaminant, established its source i.e. the board and a likely course by which it had arrived. A problem such as this is resolved by a combination of skill and experience in the collection and sifting of information and the use of sophisticated analytical techniques. It also requires close, effective liaison with the ink manufacturer's customer.

Acknowledgment

Dr W.Reid of the FRA.

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M. Morcillo et al, continued from p.28

additivity of effects? Does there exist a synergic or inhibiting effect because of the incorporation of the second contaminant? In order to answer these questions, Table 3 shows the values of the relation.

Corrosion for a determined combination of

$$R = \frac{\text{contaminants}}{\text{contaminants}}$$

Sum of the individual corrosions of each of the contaminants acting independently
 for the different combinations considered. As can be seen, the value of R stays very close to the unity, with frequent values of 0.7 and 0.8 suggesting a quasi-additive effect.

Table 3

R values for different combinations of contaminants after 485 hours of exposure in a humidity condensation chamber.

Chloride contamination, mg/m ²	Sulphate contamination, mg/m ²				
	50	100	250	500	1000
5	0.9	1.0	0.8	0.8	0.8
10	1.0	0.7	1.0	0.8	0.8
20	1.0	0.9	1.0	0.8	0.9
50	0.7	0.7	0.8	0.8	0.9
100	0.7	0.7	0.8	0.7	0.6
500	1.0	0.8	0.8	0.8	0.7

Conclusions

The presence of hydrosoluble contaminants (FeSO₄ and NaCl) in the steel/varnish interface promotes blistering of the coating and under film corrosion of steel.

The morphology of blistering shows differences in accordance with the type of contaminant existing in the interface. The ferrous sulphate tends to produce a large number of small blisters, whereas the sodium chloride induces few but large blisters.

The iron corrosion products formed under the varnish coating are similar to those which form on the uncoated steel exposed to the atmosphere.

The controlling factor for the underfilm corrosion process on uncontaminated surfaces is not the arrival of oxygen to the steel/varnish interface. The fact that corrosion significantly

increased with interfacial surface contamination suggests that the ionic conduction resulting from the saline deposit in the interface, is the real controlling factor. However, in the case of highly contaminated interface, underfilm corrosion seems to be governed by the diffusion of oxygen through the varnish film.

For this particular steel/varnish system, it is not possible to deduce the existence of critical thresholds of surface contamination for corrosion beneath the film and blistering of the coating to take place. Such low concentrations as 5mgCl⁻/m² or 50mgSO₄²⁻/m² are quite enough for the development of both phenomena, increasing in intensity with the surface concentration of contaminant.

As regards to the joint action of both contaminants the corrosion data suggest a quasi-additive effect.

Acknowledgements

The authors would like to acknowledge to the Comisión Interministerial de Ciencia y Tecnología (CICYT) for the financial support to this research. Further thanks are due to Miss Mercedes Gracia, of Instituto de Química-Física Rocasolano, for the acquisition and identification of the Mössbauer spectra, and also to CROS PINTURAS, S. A. for the supply of the varnish coating.

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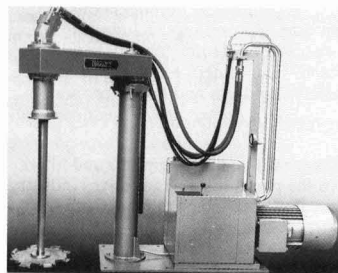
APV Mixers are widely used by the paint and printing ink industries, at all stages of manufacture. Invariably based on standard ranges, the units supplied can include special features to comply with the clients' specific requirements. Impeller shape and number, speeds of rotation and materials of construction are all selected for the particular duty. In many instances, stainless steel is used with high polish crevice-free finish. This ensures efficient, between batch, cleaning to maximise product quality and consistency. Vessel sealing is normally of the packed gland type. However, if the process involves pressure or vacuum, mechanical seal systems are fitted.

For further information Enter A401

The **DYNO Mill** range of bead mills from W. A. BACHOFFEN, has been extended to include several new models. Many additional features have been incorporated, including choice of bead retention system and option variable speed drive. Internal design improvements and a new form of agitator disc have given higher mill output, with correspondingly lower mill pressures and product outlet temperatures. Unsupervised mill operation is made possible with a new, programmable control-panel and data bank. All batches are pre-programmed individually, to control and monitor relevant process variables. Similar control of the pre-mixing operation, including charging and discharging of materials are facilitated with the **DIAMIX** range of enclosed mixers. These come from **DIAF** of Copenhagen. The Mixers have a side scraper and disperser, and use power more efficiently than conventional dissolvers. The **Glen Creston** range of dispersion equipment is strengthened by the range of **MIRALLES 3-Roll** mills. Machines are available from 1.2 metre roll lengths, down to bench top models. Process, temperature and automatic control are available.

For further information Enter A402

Eiger Torrance merge: The beginning of 1989 saw the acquisition of Torrance & Sons Ltd by the Eiger Group of companies. Over the past 10 months it was clearly obvious that the Torrance range of equipment has still a firm place in the market, and in order that the name of Torrance could be kept alive Eiger Engineering has now changed its name to Eiger Torrance Ltd. In the past 10 months orders worth more than one million pounds have been taken and these covered Hydraulic Mixers, Belt Driven Mixers, Attrition Mills, Batch Bead Mills and Horizontal Mills. More

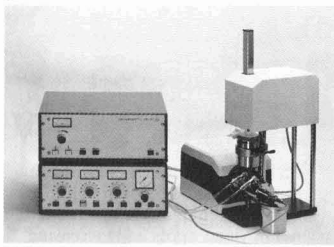


Eiger Torrance M50 Hydraulic Cavitation Disperser.

recently Eiger Torrance had designed, delivered and commissioned two major paint manufacturing plants in the U.K. and has also delivered and commissioned its first resin manufacturing plant. The range of equipment now available from the Eiger Torrance Group makes the Company one of the major equipment suppliers in the World.

For further information Enter A403

The well-known **DISPERSMAT** range of laboratory size High Speed Dissolvers now complemented by the addition of **DISPERSMAT SL** horizontal bead mills. These units, like those in the HSD range are designed for ease of use and cleaning while enabling precise, independent control of all the milling parameters. It is therefore possible to obtain accurate correlation



Fullbrook's Dispersmat SL Horizontal Beadmill and Feeding Press.

of laboratory results with those achieved on production scale equipment. The **DISPERSMAT SL** units are currently available with milling chambers of 50, 125 and 250 mls volume, and can be supplied with different levels of control and indication sophistication, by the UK Agents - **Fullbrook Systems Ltd.**

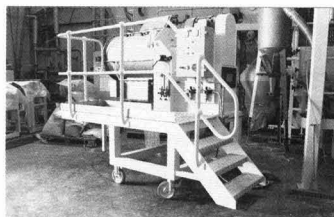
For further information Enter A404

The High Speed Disperser from **Joshua Greaves** is still the main method of producing dispersions and has many advantages - different batch sizes can be accommodated by varying the impeller diameter, for example, and the

equipment is easily cleaned. HSDs, however, are potentially extremely dangerous, but Greaves have made available a guarding/interlocking system which meets Health and Safety Executive requirements, in either IP55 or EEx'd flameproof. Most models are variable speed, ranging from 40W to 370W lab mixers and from 1.5kW to 75kW production mixers, the latter offering the option of variable speed using either inverters, belt drives or hydraulics. A new model now available is a twin shaft mixer using a variable speed 'bow-tie' paddle agitator and fixed speed disperser. For high production factories, a triple mixer design utilises a fixed speed HSD and variable or two-speed agitator, combined with a scraper/agitator and vessel. This eliminates the need to raise the head of the disperser, and pressurised discharge is also available, rendering a discharge pump unnecessary.

For further information Enter A405

Kemutec Group's comprehensive range of **GARDNER** horizontal mixers includes three new standard ranges; the 'HE', 'PE' and 'RE' Series machines.



(Kemutec's Gardner 'PE' Series Mixer).

They have the expertise to design mixers for products as diverse as dry powders, through to car body fillers, and excellent manufacturing facilities in which to build them. Working capacities are from 'Laboratory size' up to 20,000 litres. Construction can be of epoxy painted mild steel through to 316 grade stainless steel. For applications demanding the most stringent standards of hygiene, stainless steel mixers can be mirror polished both internally and externally if required.

For further information Enter A406

Marchant Brothers introduced the **VIBROMAC HYDROMIX DISPERSION SYSTEM** to the UK to get away from the "we mix everything in different pans and they all go under a 25 HP sawtooth/bow-tie/propeller bladed Mixer". The system, whether 'change pan' or 'fixed vessel' can aid

Mixing

production by virtually finishing a product in the Mixer. This is achieved with the skill of your development Chemist, the heavy duty hydraulic system giving high torque through variable speed range of the trifoil, blade is tailored to vessel walls and base. It will achieve breakdown of agglomerates and pigment wettability only previously given by Z Blade Mixers and flushings. 'Letdown' is made by secondary dispersing head. This also controls product temperature, the secondary head can also be a dissolver or turbine. Should you need to mill after mixing you should only have to refine and NOT grind.

For further information Enter A407

Milchem manufacture a wide range of Mixing and Dispersion equipment, from large production machines down to laboratory size units. Standard machines include the long established "ROTAMIX" range of Rotor Stator Mixers, HSD Mixers, change pans and vessels, constructed, in either mild steel or stainless steel. The most recent development is the "BATCHRANGER". Probably the most efficient Dispersion Mixer on the market today. The unique design offers remarkable savings in process time, energy and capital cost when compared with conventional HSD type Mixers. Trial facilities are available on most machines.

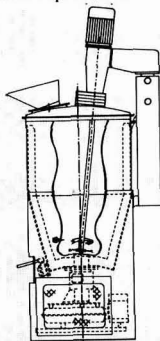
For further information Enter A408

Moritz Industrial Turbo Mixers are superior to most other stirrers, which merely rotate the mass without effecting true mixing. This superiority is due to a negative pressure around the impeller, which draws the product to the centre. It is then thrust against the stator where the current divide and completely intermix. The product rises against the vessel perimeter and is drawn down to the centre again, this continuous mixing

gives a completely homogeneous product. Advantages include: Cuts in process time. Homogeneous results, Easily maintained, Meets rigorous safety standards and Power economy.

For further information Enter A409

Dispersion of bulk pigments and fillers for the paint, ink and adhesives industry has always posed problems of time, particle size, power usage and health/safety. The move towards fixed vessel design and multi-agitator systems reduces these problems dramatically. High speed dispersion provides an efficient means of incorporating a powder into a liquid, however, it has disadvantages: High power consumption/unit volume, 'Dead' spots in the vessel, Dust problems whilst feeding. The PMD and PMD-VC (variable capacity) from **Netzsch Mastermix** provides a solution to these problems and many more. The patented design incorporates both high speed toothed disc disperser, together with a slow speed cage stirrer, fitted with PTFE wall scrapers, the combined



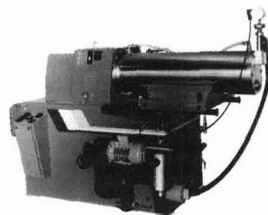
Netzsch Mastermix PMD.

system has the advantages of; lowering power consumption per unit volume, ensuring efficient particle size reduction by ending 'dead' spots and increasing

the efficiency of the high speed blade and dispersion time reduction due to intense mixing action.

For further information Enter A410

A 50 litre horizontal Supermill Type 50 EHP with a recently introduced new geometry shell is available from **OBS Machines Ltd** of Milton Keynes. The Supermill EHP features an extended process chamber with more grinding discs per shell volume and offers a



OBS Supermill EHP.

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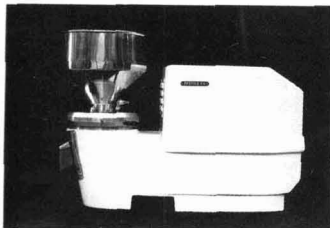
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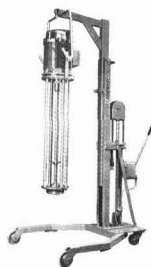
Russell Finex have extended the range of their variable speed RUSSELL-COWLES Dispersers. Machines are now available in variable speed up to 100hp. A 15hp unit has also been introduced to fill the gap which currently exists between pilot plant and large scale production models. All of the well established Russell-Cowles features have of course been

incorporated in the design of these new machines including the patented box bridge construction (this enables the machine to run very quietly and smoothly) and the MPD concept, (which gives maximum power delivery over the whole speed range).

For further information Enter A413

Silverson Machines manufacture a complete range of high shear rotor/stator mixers, disperser and disintegrators for use on batch or in-line operation. Machines are available for batch operation for 1 litre to 10,000 litres. The types of operation in which they are most widely used and

Silverson Model BX 20hp Batch Mixer on a Mobile Hydraulic Stand.



recommended in the paint industry are the single stage cold cutting and solution of resins into solvent and the dispersal and homogenising of pigments and fillers. The two operations may take place simultaneously, making it possible, for example, to produce a finished emulsion, undercoat or high gloss paint in one operation. For the more refractory pigments the Multishear Mill, a multi-rotor/stator in-line mixer is available.

For further information Enter A414

The type of mixers available from **Sulzer (UK)** are static mixers. Static mixing is achieved by passing the materials to be mixed through a fixed geometric structure which splits the stream of material into numerous parts as it passes through and then reunites them with a different part of the stream. The result gives a degree of mixing which can be predicted mathematically, so that the required degree of mixing can be achieved simply by inserting the required number of mixing elements. A high degree of homogeneity can be achieved within a mixer housing which is twice its diameter in length. The mixer housing is flanged for easy insertion into existing pipe runs.

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Standards News

Compiled by Peter Munn,
Surface Coating Consultant

□ A proposal has been made to the European Standards Organisation (CEN) to introduce a Standard to cover "The Protection of Steel Structures from Corrosion by Organic and Metallic Coatings".

□ Proposals for the preparation of CEN Standards for "Powder Organic Coatings on Aluminium for Architectural Purposes" and "Liquid Organic Coatings on Aluminium Alloys for Architectural Purposes" have been agreed.

□ A "Draft for Comment" has been issued covering the BS Code of Practice for the use of Profiled Sheet for Roof and Wall Cladding on Buildings. This is a revision of BS 5427:1976. It contains recommendations covering the expected lifetimes of coating materials on commonly encountered cladding materials.

□ Attention is drawn to the "Qualicoat" system as a certification basis for coatings for aluminium. Members experience

with this system is sought.

Comments on these Standards should be addressed to Peter Munn at Priory House.

BSI News

BS 7079 : Part A1 : 1989

Preparation of steel substrates before application of paints and related products.

Group A. Visual assessment of surface cleanliness.

Part A1. Spec for rust grades and preparation grades of uncoated steel substrates after overall removal of previous coatings.

BS 7079 : Part C1, C3, C4 : 1989

Preparation of Steel substrates before application of paints and related products Gr C. Surface roughness characteristics of blast-cleaned steel substrates.

Part C1. Spec for surface profile comparators for the assessment of abrasively blast-cleaned surfaces.

Part C3. Method for the calibration of surface profile comparators and for the detern of surface profile using a focusing microscope.

Part C4. Method for the calibration of surface profile comparators and

for the determination of surface using a stylus instrument.

BSI publications are available from:
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Organotin, continued from p.39

suggested a complete ban on triorganotins in antifoulings and for all marine applications, including treatment of nets used to confine farmed fish in sea lochs. This measure would of course avoid the problems of collecting and disposing of TBT wastes, but at present would involve considerable extra costs to shipowners because intervals between drydockings would have to be reduced to allow for the shorter effective lives of TBT-free antifoulings. It was suggested that whilst it might be necessary to use cuprous oxide based antifoulings, there would be no need to revert to traditional rosin types; instead modern polymers with much improved film integrity could be used. Such polymers can be formulated to have a suitable degree of water solubility, thereby retaining the "self-polishing" properties of current organotin types. There is still plenty of scope for paint technologists in the marine paint field!

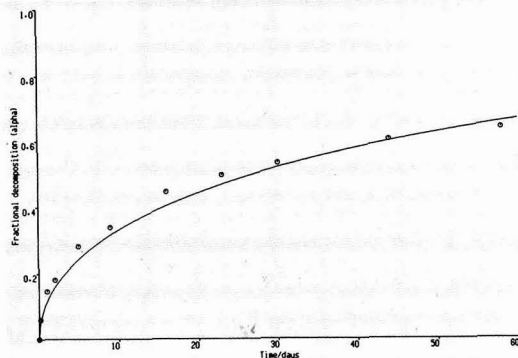
T. A. Banfield ■

P. Gardner *et al*, continued from p.17

fit" for these data was again to an equation of the form mentioned previously (type D3 in sharp *et al*'s notation⁶) and the rate constant was $0.00225 \pm 0.00006 \text{ day}^{-1}$. This figure is of the same order of magnitude as the result for the paint film and clearly implies that the binder in the cured film offers little protection to moisture ingress. Bishop⁴ has also measured the rate of conversion of pure dihydrate under similar conditions (80–90%RH) to those reported here by a gravimetric method and his results are comparable with ours *eg*. Bishop found $\alpha=0.39$ after 7 days.

Figure 4

Fractional conversion (α) vs. time for zinc phosphate dihydrate in an alkyd binder; the full line is the rate equation (see text) and the points are experimental results.



The rate of hydration of the dihydrate, either in a paint film or as a pure substance, will depend on the partial pressure of water (or relative humidity) in contact with the material. When the partial pressure is the thermodynamic equilibrium pressure, the net hydration rate is zero. At 20°C, the equilibrium partial pressure⁷ is ca.15mmHg which corresponds to a relative humidity of ca. 85%. Consequently at relative humidities below 85 \pm 5%, zinc phosphate dihydrate will not hydrate; this figure has implications for the storage conditions of bulk samples of this pigment.

Acknowledgements.

This work was supported by the MOD (PE).

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Activities of the European Federation of Corrosion

by the National Council of Corrosion Societies, 1 Carlton House Terrace, London SW1Y, 5DB, UK

The National Council of Corrosion Societies is a body — on which Occa is represented by our Honorary Editor, John Taylor — formed in the UK for the purpose of co-ordinating activities of those scientific and technical societies concerned with corrosion and its protection in the UK. One function of the NCCS is to appoint and support where necessary delegates to the Working Parties (WP) of the European Federation of Corrosion (EFC). These delegates meet in the UK annually to report to the NCCS and other interested scientific and technical institutions on progress within the EFC. The present report is a summary of progress made for the year ending April 1989.

In October 1988 the WP on Inhibitors organised a one-week course, which included practical sessions, on corrosion inhibitors in Frankfurt. This was the second such event. Reports on special topics in the inhibitor field continue to be produced by the WP and the one currently under consideration originates from Poland and concerns inhibition in refinery processes.

A new WP on Computer Based Information Systems in Corrosion held its first meeting in 1989 and is to produce an inventory of information systems available, or under development, in Europe. This will be followed by a consideration of how to combine and interface these systems. good liaison has been established with similar activities in the USA.

A WP on microbial corrosion has held a workshop meeting in Portugal and the proceedings have now been published. A study is being made of the economic effects of microbial corrosion in various European countries. There will be a mini-symposium during the Biotechnology Congress in 1990.

Physico-chemical methods of corrosion testing form the subject of another WP. A booklet on "Guidelines on Electrochemical Corrosion Measurements" is in an advanced stage of preparation for publication by the UK Institute of Metals as part of a series of EFC publications. This WP is also engaged in comparing methods to determine polarisation characteristics and common monitoring using various commercially available instruments.

The Marine Corrosion WP has also produced a guidance document on General Guidelines for Corrosion Testing of Materials for Marine Applications and has initiated a cooperative natural sea water exposure test programme.

Two workshop type meetings have been held by the WP concerned with the Corrosion by Hot Gases and Combustion Products. One was on corrosion in waste incineration and gasification plants and the other on new fundamentals in scale

growth — thus embracing practical and theoretical aspects of WP title. It is the intention to include the topic of corrosion in Air Pollution Control Equipment within the WP activities for the future. This WP has agreed to cover corrosion and protection in flue gas desulphurisation plant and a subgroup has been formed to coordinate these activities.

The WP dealing with corrosion in the Nuclear Industry met at Harwell in October 1988 when 19 technical presentations were made covering ten topic areas. The proceedings of a meeting held at Karlsruhe in 1987 are now being published by the Institute of Metals in the EFC series.

The broad field of corrosion education is covered by the WP of that name and has recently produced, through the European Corrosion Education Foundation, a film and associated video with the title "Corrosion prevention by changing the environment". The next film will deal with the subject of selection of corrosion resistant materials. A revised edition of the Corrosion Education Manual will appear shortly and a Manual of Corrosion Experiments will form part of the EFC series being produced by the Institute of Metals.

The WP concerned with Surface Science and Mechanisms of Corrosion and Protection has successfully conducted the experimental part of a round-robin exercise on the surface analysis of thin aluminium oxide films. This work received partial support from the Community Bureau of References of the Commission of the European Communities. The results were published at the UK Corrosion/Eurocorr 88 conference in the UK last year.

One of the newer WPs is concerned with the corrosion of reinforcement in concrete. This now has an ambitious working programme which will be developed through sub-groups concerned with non-destructive testing, potential mapping, ac impedance techniques, cathodic protection and rehabilitation techniques.

A WP on stress corrosion test methods that operated for many years and contributed towards the development of ISO standards has now been reconstituted under the title of Environment Sensitive Fracture and its new programme will be announced shortly.

These various WPs draw membership from some nineteen European countries and thus provide a vehicle for exchange of experience and agreed recommendations for combating corrosion.

Further information on UK participation in the EFC and its WPs can be obtained from the Secretary of the NCCS: Dr. A. J. Collins, Houseman (Burnham) Ltd, The Priory, Burnham, Slough SL1 7LS, UK. Tel 0628-604488. ■

Newcastle Section Student Seminar
PAINT MANUFACTURE

24 April 1990, Durham University

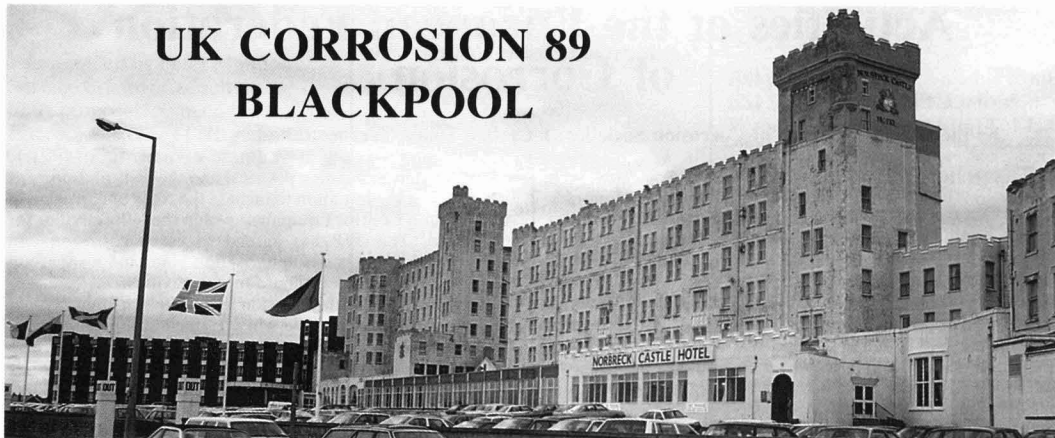
Contact OCCA for further details

Joint Symposium OCCA/SBPIM
PRINTING INK FOR THE '90s

22 March 1990,
Grand Hotel, Birmingham

Contact OCCA for further details

UK CORROSION 89 BLACKPOOL



A Great Success

Over 925 day delegates attended a 3-day conference held on 8-10 November 1989 at the Norbreck Castle Hotel, Blackpool, organised by the Corrosion Engineering Association, the jointly-owned arm of the Institution of Corrosion Science and Technology and the National Association of Corrosion Engineers. There were 24 technical sessions and 66 papers presented. Concurrent with the conference 500 additional visitors attended an exhibition featuring 71 stands showing a wide selection of products and services concerned with fighting corrosion.

The Conference:

Of special interest to Coatings Technologists were the papers in the sessions under "E5 - Coatings and Linings" presented on 9 and 10 November. On 9 November Mr R. S. Hullcoop, Consultant, High Wycombe, chaired the first day. Mr R. G. Vyse, Technical Manager, Development of British Steel, Shotton Works, opened the morning session talking on "Pre-painted strip for the building and construction industry - products and performance". In his talk he discussed the growth of pre-painted strip to the Building and Construction industry in Europe from 1983-88 and gave a breakdown of market share in the UK for pre-painted strip for roofing and walling applications in Industrial and Warehouse buildings from 1976-88. The types of organic finishes currently available to the

Building and Construction Industry were discussed. Mr Vyse then presented a second paper on "Some reasons for poor performance of pre-painted strip in roofing and cladding applications".

The second paper of the morning was presented by Mr P. D. Haworth, Technical Manager, Freeman Chemicals Ltd, Paint Division, Deeside, who spoke on "Answers to technical problems associated with overpainting cladding panels". The use of pre-coated cladding panels has increased dramatically in the last fifteen years. With this increase there has been a need to overpaint the original coating. This paper discussed the reasons for overpainting of cladding and the choice of a coating for a long-term solution.

The third paper of the morning session was presented by Mr J. M. B. Asher, Managing Director, Crown Industrial Products and Mr E. N. Pratt, Technical Manager, Crown Protective Coatings, talking on "Repaint systems for cladding". Pre-painted cladding is a very durable building material designed to give a long serviceable life. Even so the product will deteriorate with time.

This deterioration takes place in four phases but timely maintenance with a specialist coating system can prolong the effective life of the cladding. The choice of repaint system is crucial in ensuring effective maintenance for the cladding. Standard systems are not suitable for the unique coating problems presented by cladding. Single pack moisture cured urethane systems offer numerous advantages. They give excellent chemical and UV resistance and can be applied in less than favourable weather conditions. Research has shown that the use of a specialist repaint system is the most economic means of prolonging the effective life of a cladded building.

The final talk of the morning was presented by Mr D. M. Howell of W. S. Atkins Structural Engineering who spoke on "Specifying colour coated cladding - taking a realistic view". The history and development of colour coated cladding was outlined together with a brief description of the product from manufacture to installation. The requirements of specification for the product were discussed and the key items to be included in a performance specification were outlined. A general

E5 Coatings and Linings Discussion (L to R) R. S. Hullcoop, J. Asher, R. G. Vyse, D. Howell, E. N. Pratt and P. D. Haworth.



comparison of the performance of various generic coating types were given and the current industry standards discussed.

Following lunch the Keynote Lecture to the UK Corrosion was given by Fred Palmer of BP Engineering who spoke on "The life and times of a practising corrosion engineer". In his lecture Fred gave a lighthearted talk about his career both in the Paint Industry for 19 years and latterly in the Oil Industry, also for 19 years.



Fred Palmer presenting the ICorrST Keynote Lecture.

Fred, a Lancastrian, obtained a degree in Chemistry from Liverpool University in 1952 and joined Goodlass Wall as a research chemist in their Liverpool Laboratories. In 1956 he transferred to the Technical Service Division and in 1967 moved to Goodlass Wall's London office. In 1971 he joined BP and travelled around the world on troubleshooting, specification, etc., being involved with Fortes, Magnum, Sullem Voe and the Alaska Pipeline. He has been actively involved with the ICorrST for the last 20 years and has held a variety of senior positions within the Institution.

The final talk of the day was given by Mr Lukey of the BSI who spoke on "The protective coatings contractors scheme". In his talk he described the Quality Assessment Schedule to BS5750 Part 2, relating to Protective Coating Contractors in the Building and Construction Industry. This schedule was launched in April 1989 - Document QAS/5010/348. He then went on to discuss the scheme. First a questionnaire is completed, application is invited, assessment is then undertaken followed by registration. He also suggested that paint inspection firms could also be assessed under this schedule. For further information on this scheme contact: BSI Quality Assurance, Business Development, PO Box 375, Milton Keynes MK14 6LOL, UK.

On 10 November Mr E. Carter of Cookson Laminox Ltd chaired the first

session. Mr I Thompson and Mr C. Temple of British Gas presented a paper on "The relationship between cure and performance of single pack moisture cured urethanes". Moisture Cured Urethane (MCU) paint systems are being used increasingly for new construction and for maintenance painting. The popularity of these materials is partly due to their weather tolerance which allows them to be used under adverse environmental conditions, but also to their very short overcoating time which makes it possible to apply a complete three coat system in a single day. A number of problems have recently been identified mainly related to intercoat adhesion weakness which, in some cases, has led to coating detachment. This paper identified some of the conditions which can contribute to adhesion failure in particular the effect of environmental conditions during application and curing, the chemical changes which occur in the paint as it ages in the container and the effect of sunlight as the material cures. Where possible, the paper indicated precautions which should be taken to reduce the incidence of adhesion problems.

Mr B. C. Goff, of Pipeline Induction Heat Limited, then spoke on "The coating of pipeline field joints: The state of the art and a look to the 1990's". The development of pipeline coatings in the 1970's and 1980's has been technically very significant. A wide range of anti-corrosion coating systems have been used ranging from the traditional coal tar and asphalt coatings to the more sophisticated systems such as fusion bonded epoxy powder, polyethylene and multi-layer insulation systems. Whilst the pipeline coating plants have been developed to apply these sophisticated coatings to the clients strict specifications, the client has to some extent not placed the same emphasis on strict specifications for coatings applied to the field joint. In his paper Mr Goff discussed the application of field joint to pipelines during the early/mid 1980's. He then reviewed the current field joint coating systems and application techniques with emphasis on the newer multi-layer insulation systems. For the 1990's he outlined the new breed of multi-layer polypropylene systems and ethylene propylene dimonomer elastomeric abrasion resistance coatings.

For the second session on 10 November Mr A. Tong of ITI Anti-Corrosion Ltd chaired the meeting. Mr F. C. Porter, Consultant, spoke on "Alloyed zinc coatings - a

review". The performance of zinc has been so reliable and well documented that most coating methods - spraying, hot dipping, electroplating, mechanical coating and sherardizing - traditionally have started with a reasonably pure zinc. In recent years, an interest in alloy coatings has developed to obtain still longer lives for zinc coated products or, in some cases, to reduce the cost of the coating materials by using thinner alloy coatings of comparable performance to thicker pure zinc coatings. This paper indicated the major alloy developments, the types of coating process to which they are applicable and their corrosion-resistant properties.

The final paper of this last session was presented by Mr H. Tomes of North Point Powder Coating Ltd on "Architectural coatings offer long-term durability on zinc/aluminium components". Over the last 30 years two main coating technologies have become established for the high performance finishing of Architectural Aluminium, Polyester powder coatings and Fluorocarbon wet paint (PVF2). This paper addressed and compared the key features of these two alternative systems and examined the varying levels of acceptance in major world markets. The importance of Architectural finishing standards was also discussed with particular relevance to the market impact of the two technologies.

The above described papers are available in a 3-volume series from ICorrST. Vol 1 (8 November), Vol 2 (9 November), Vol 3 (10 November). The price for the individual volume is £20, the price for the 3-volume set which contains over 60 papers is £50. For further information contact: ICorrST, PO Box 253, Leighton Buzzard, Beds LU7 7WB, UK.

The Exhibition:

Companies showing surface coatings, services and technologies included:

ACM Instruments featured their Electrochemical Interrogation Equipment: multiple electrode cells responding to various electrochemical techniques e.g. environmental testing of multiple painted samples.

For further information Enter A301

Blastline Ltd highlighted a range of blast cabinets, blast rooms and blast machines.

For further information Enter A302

Bristol Metal Spraying and Protective Coatings Ltd featured their wide range of anti-corrosion coatings: Zinc and Aluminium Coatings, Limpetite synthetic rubber urethanes, Glass Flake and coatings for reclamation work.

For further information Enter A303

C & W Specialist Equipment featured their popular Compact SF/450 saltspray chamber and the AB6 humidity cabinet.

For further information Enter A304

CAPCIS - Corrosion and Protection Centre Industrial Services:

Multi-disciplinary teams within CAPCIS specialise in materials selection and testing, corrosion investigation, corrosion prevention, corrosion monitoring and failure investigation.

For further information Enter A305

Complete Corrosion Control Ltd highlighted their consultative service on grit/shot blasting and specialist coatings.

For further information Enter A306

Corrocoat Ltd featured their range of specialist anti-corrosion coatings for refurbishment of severely corroded components and the protection of new equipment. Their range includes tank linings, vessel linings, pump and valve repair systems, etc.

For further information Enter A307

Cortest Laboratories highlighted their contract corrosion testing, consultancy and applied research.

For further information Enter A308

Croda Paints Ltd highlighted a wide range of high performance coatings

For further information Enter A309

Crown Protective Coatings exhibited two new products - Cemguard - the complete concrete protection system and - Colour Match - the universal tinting system for small quantities of specialist protective coatings.

For further information Enter A310

CSMA highlighted their Consultancy Service in all areas of surface and materials analysis including SIMS, ESCA, Auger, TEM, SEM, XRD and Optical Microscopy.

For further information Enter A311

Dirk Group of Companies featured their Blastgrit available in 5 grades.

For further information Enter A312

EG & G Instruments demonstrated a range of electrochemical instruments.

For further information Enter A313



Packed Norbreck Exhibition Hall.

Electro-Physik displayed their full range of Minitest portable coating thickness gauges, Porotest holiday detectors and the Mikrotest range of magnetic dry film gauges.

For further information Enter A314

Freeman Paints Division highlighted their systems for overcoating cladding and their full range of high performance coatings for structural steel, concrete floors, roofs and walls.

For further information Enter A315

Hesco displayed coatings for new or old concrete structures in a wet or dry state. A new development was "Rhessinite A/Puf" - a highly flexible corrosion resistant, flame retardant coating for flue ducts.

For further information Enter A316

Hodge Clemco Ltd featured their range of surface treatment and finishing equipment.

For further information Enter A317

Inventive Machines Europe Ltd featured their vacuum blasting systems.

For further information Enter A318

Jotun-Henry Clark featured a wide range of products for corrosion control including "Jotamastic-87" epoxy coating for steel. "Wintergrade Jotamastic-87" for application down to -15°C - "Baltflake", glass-fibre polyester. "Navitar AS" solvent-free epoxy-tar coatings ideal for splash zones.

For further information Enter A319

Macpherson Paints, Heavy Duty Division, featured "Temaflor" their new range of high performance industrial floor products and "Temaclad" their range of maintenance coatings for coil-coated substances.

For further information Enter A320

NICC Ltd featured their consultancy and materials selection service for a broad range of high quality corrosion protection products for onshore and

offshore.

For further information Enter A321

NNC Ltd highlighted their consultancy service in protective coatings and launched at the exhibition an instrument that measures soluble salts on surfaces prior to painting - the SCM400 - Salt Contamination Meter.

For further information Enter A322

Novamex Technologies highlighted their aluminium finishing, conversion coatings and pre-treatment technology for coil-coating.

For further information Enter A323

Prodorite Ltd featured a complete range of anti-corrosion and chemical resistant coatings and linings including corrosion coatings and deck finishes for oil platforms and rigs, pipelines and concrete structures.

For further information Enter A324

Sigma Coatings Ltd featured their wide range of products for the protective coatings and offshore markets. On show was the new prefabrication primer: Sigmagweld MC for Mig/Mag, Submerged Arc, and MMA welding procedures - a breakthrough in the development of weldable shop primers.

For further information Enter A325

SPE (International) Ltd featured their Mobile Dust Free Blast Cleaning Equipment for steel SA 2 1/2.

For further information Enter A326

Technology Offshore Onshore Ltd featured their consultancy supervision and inspection in all aspects of protective coatings including fire proofing and insulation.

For further information Enter A327

W & J Leigh & Co. featured their wide range of coatings for steel protection including Firetex intumescent coatings and Resistex one-coat primer/finish incorporating highly effective anti-corrosive agents for interior steelwork.

For further information Enter A328

Winn & Coales (Denso) Ltd had on show the latest advances in their anti-corrosion range. Also featured was their new acquisition Archo Ltd with a display of their effective lining products.

For further information Enter A329

UK Corrosion '90 will be held on 29-31 October 1990 at the Sandown Exhibition Centre, Esher, Surrey.

P. J. Fyne ■

Organotin antifouling compositions:

The impact on shipowners and shiprepairers of existing and proposed environmental legislation

A Seminar on the above subject was held at the General Council of British Shipping, London, on 25 October 1989. It was jointly organised by the Marine Paint Forum of British Maritime Technology Ltd and the Oil & Colour Chemists' Association, and attended by 65 delegates.

Organotins, chiefly tributyltin compounds, have been used in antifouling compositions since the early 1960's. At first they were used to boost the toxic effects of cuprous oxide and later as the sole toxin. The main development during the last 15-20 years, however, has been the use of binders containing organotin groups, eg tributyltin acrylate or methacrylate polymerised with methyl methacrylate. Such copolymers have a high tin content and are slowly hydrolysed in water releasing tributyltin groups; the residue of the polymer is water soluble, and this process exposes fresh surfaces to the water. These antifouling are often called erodable or self-polishing. In practice they have proved both technically and economically successful on all types of vessel – yachts, merchant ships and warships. Unfortunately it has become apparent in recent years that organotin concentrations in some coastal waters near yachting marinas and in landlocked waters such as the Norfolk Broads, have become high enough to interfere with reproduction and growth of many shellfish, including oysters and mussels. The toxic effects have also been observed near fish farms where organotin preservatives were used on nets and other equipment.

The first paper, by M. Waldoock of the Ministry of Agriculture Fisheries and Food, outlined the problems and produced evidence that very low concentrations (a few ng/l) of TBT in fresh or sea water are sufficient to cause adverse effects on both European and Pacific oysters. Following restrictions on the use of organotin antifouling on small boats in 1986 and a complete ban in 1987, he was able to confirm that TBT concentrations in shallow semi-enclosed waters had fallen in 1988 and 1989, and that commercial production of both types of oyster has again become possible. Preliminary studies of the effects of TBT antifouling on seagoing ships in normal operation show no adverse effects on inshore marine animals and plants, although dry docking

procedures may lead to high concentrations of TBT in waste water and this poses problems.

The second paper, by R. Abel of the Directorate of Environmental Protection of the Department of the Environment, covered the legislation introduced to control TBT in coastal waters. The first UK Regulations were introduced in 1986 and strengthened in 1987; antifouling compositions containing triorganotins are not permitted on vessels under 25m in length, and may only be supplied in containers of 20 litres or more which must be labelled to show restricted use. Similar regulations apply in France and are under consideration by the European Community. An environmental quality standard has been set for TBT at 2 ng/l for the protection of salt water life, and this applies to discharges from drydocks when antifouling are washed down or removed from ships' bottoms.

The third paper by R. W. Adams and J. F. D. Stott of the Analytical Group of CAPCIS (Corrosion and Protection Centre Industrial Services, UMIST, Manchester) dealt with analytical methods required to measure very low concentrations, down to 1 ng/l, of organotins in water. The two most generally used techniques – gas liquid chromatography and graphite furnace atomic absorption spectrometry – are not capable of measuring such very low values so the samples are first concentrated by solvent extraction (eg. with methylene chloride) followed by evaporation, thus concentrating the TBT about 5,000 times. Biological techniques using oyster spat grown in the water for several months were also described; analysis of the animals for TBT gives an integrated figure for the long term level at the site.

The fourth paper by C. C. Hamlin of Devonport Management Ltd (the former Royal Navy Dockyard) dealt with the procedures developed to deal with contaminated waste water produced in dry dock operation by (i) high pressure washing of the hulls of vessels coated with TBT antifouling, (ii) cleaning hulls to remove old TBT antifouling, and (iii) washing down docks after spraying TBT antifouling to remove overspray before resuming normal work. The methods have been in routine use at Devonport for about 20 months and could be adapted to almost any dry dock. In brief three steps are involved: (i) Retaining the

contaminated water in the dock, (ii) Pumping this effluent from a sump in the dock bottom to a road tanker at the dockside, and (iii) Removal of the effluent by tanker to a suitable licensed waste disposal site. Obviously precautions must be taken to avoid diluting the contaminated water with clean water, in order to minimise the volume for disposal. Initial use of the system with a large vessel produced 18,000 gallons TBT effluent and frigates have been washed down with 8,000 gallons. Volumes of this order are easy to transport, and at Devonport the waste disposal site is only 5 miles away. The speaker gave a rough estimate of the cost of these operations at £5,000 per docking.

The final paper, by D. M. Allison of the Chief Naval Architects Department, Ministry of Defence, concentrated on the measures to be undertaken in shipyards to control harmful discharges arising from the use of TBT antifouling. A draft Code of Practice has been prepared. Many of the points had been covered in the previous paper, although some factors attracted a different emphasis – for instance one dockyard had been obliged to transport contaminated waste water 200 miles to a licensed disposal site, as compared with only 5 miles at Devonport! This had led to a system of storing and re-using wash water several times before disposal. It appears that the cleaning down of hulls by high pressure water washing offers the greatest problem, the application of TBT antifouling or their removal during repairs not offering serious additional hazards. Solid waste, eg TBT contaminated blasting grit, does not offer any greater difficulty than other toxic solids, and can be disposed of at licensed sites.

In the discussion questions of drydock procedures and costs attracted much attention. In the case of large drydocks undertaking major refitting and repairing of large ships – work taking months or even years – the extra costs of containment and disposal of toxic wastes are only a small part of the total cost of the work. On the other hand, for smaller commercial docks handling 2 or 3 ships per week the extra costs would be proportionately much greater and it is possible that such docks might not be prepared to accept ships with organotin antifouling. A House of Lords Select Committee has in fact

Continued on p.34

Pigments for Inkmakers

by J. D. Sanders

Publ. SITA Technology

Price £45 (hb), 255pp ISBN 0-947798-07-02

This book on organic pigments lays emphasis on the influence of the chemistry of the pigments on their properties in printing inks.

The introductory chapter is on definitions and terminology, the differences between pigments and dyes, distinctive features of organic and inorganic pigments and the classification of organic pigments into pigmentary colours, metal salt pigments and lakes.

The next chapter on colour and chemical constitution gives a lucid explanation of how colour arises in organic pigments — the chemistry of the aromatic azo compounds and how substituent chemical groups can modify the hue and other properties.

Seven chapters deal with the chemistry and properties of the pigments in the various pigment groups, azo, phthalocyanine, basic dye complex and high performance pigments. Reflex blue, pigment green B and phloxine toner are also covered.

Azo pigments are given a detailed treatment starting with a section on the chemistry of the coupling process including a practical example of the manufacture of an arylamide yellow pigment. This leads on to the chemistry and properties of the arylamide yellow and diarylide yellow and orange pigments and finally the red azo pigments going through simpler red azo, arylamide reds, benzimidazole and azo metal salt pigments.

For each pigment group the format is well organised taking the reader through the constitutional aspects and detailing the effects of chemical constitution on pigment properties. These include the influence of molecular weight and structure, substituent chemical groups and metal salt-forming groups on the hue, tinctorial strength, light fastness and resistance properties of the pigments. General properties and uses are outlined for each pigment group and individual pigments in each group.

A lengthy chapter on the phthalocyanine pigments covers history and chemistry of phthalocyanines, the principal chemical and physical modifications that are encountered commercially and the manufacture of the different types.

There is a chapter on basic dye complex pigments describing the basic dye components, complexing agents and manufacture.

The chapter dealing with high performance pigments opens with the azo condensation pigments outlining the chemical constitution and reaction sequences in the manufacture of a high performance yellow pigment. Quinacridone and dioxazine pigments and the more highly specialised pigments including thioindigo, isoindolinone, indanthrone blue and perinone orange pigments are described.

A short chapter on flushed pigments discusses the advantages and disadvantages of these materials from

economical and technical standpoints. The manufacture of a flushed pigment is described and uses reviewed.

The last three chapters are concerned with stabilisation of pigment dispersion, a summary of chemical factors that are responsible for the characteristics of each pigment group and tables summarising pigment resistance properties according to chemical type. Here, as in the rest of the survey, the pigments are referred to by their Colour Index numbers.

Stabilisation of pigment dispersion begins with fundamental information about the dispersion process and goes on to describe the techniques used to control the dispersability and the role of the surfactants in dispersion stabilisation. In this connection, the information on the use of "built-in" chemical groups and bridging molecules as sites for pigment and surfactant linkages, should be of particular interest to the inkmaker.

How chemical constitution influences properties is a continuing theme. The author deals with the constitutive aspects and the chemical structure of the pigments in a clear and informative manner. At the same time he draws on a wide experience of the technical properties and performance characteristics of the various pigments in paste and liquid ink systems. This approach should be conducive to a better understanding of pigment technology for those concerned with ink research and development, ink formulation and the investigation of technical problems.

The book should be a welcome addition to the inkmaker's library and a useful reference source for those engaged in allied industrial fields. This book is priced for the specialist market and for the student who will find it instructive and informative, I recommend their technical library to purchase a copy.

G. Hutchinson ■

Polymer Processing

by D. H. Morton-Jones

Publ. Chapman and Hall 1989

Price £16 (pb), 260pp ISBN 0-412-26700-4

This book is easily read and as the author states in the Preface, "the reader may be an established student engineer, who will not require detailed chemistry, or may be a chemist. . . ." The book is aimed at undergraduate and postgraduate students who require a general overview of the field of polymer processing in a single assimilated volume and would therefore be of interest to any paint technologist wishing to know about the technology of the plastics industry.

The sections pertinent to paint are, Chaps. 1 which gives a quick, albeit good account of some of the types and properties of polymers. Chapt. 2 which could be a useful starter into the consideration of the various types of viscosity encountered in paints and resins. Chapt. 14 gives an overview of the technology associated with the properties and production of P.V.C. and Plastisols.

The remainder of the book is concerned with the properties and production of plastics and rubbers.

However, anyone using the reaction and mathematical formulae should check them as there are one or two errors.

J. G. N. Smith ■



Long-serving members

In the December General Secretary's column I drew attention to the work being undertaken to identify those of our members whose record of continuing membership extended over twenty-five years. The members so far identified have exceeded our most optimistic estimates and 441 have been identified as having continuous membership for over twenty-five years. This role of honour, headed by Dr Stern of the London Section, should, and I am confident will, be recognised by the Association in an appropriate manner. In the meantime, I am pleased to record the names of the fifty longest serving members who are ranked in descending years of service.

Stern, H. J. (London)
 Idle, H. A. (London)
 Hall, A. W. (Thames Valley)
 Schollick, F. (London)
 Diamond, H. (Midlands)
 Roe, D. E. (London)
 Gillan, J. G. (Manchester)
 Healey, A. C. (London)
 Stoyle, F. W. (Irish)
 Bruce, K. D. C. (London)
 Collings, A. G. (London)
 Leach, R. H. (London)
 Wilson, W. F. (London)
 Lock, A. B. (London)
 Jacob, B. (Thames Valley)
 Holbrow, G. L. (London)
 Polaine, S. A. (London)
 Ward, G. (Natal)
 Brooks, L. J. (London)
 Star, D. E. (London)
 Archer, H. (Manchester)
 Young, C. H. (London)
 Hughes, F. D. (London)
 Taylor, J. R. (Bristol)

Davidson, R. R. (London)
 Gidvani, B. S. (London)
 Mitchell, H. A. (Bristol)
 Hancock, W. G. (Transvaal)
 Worsdall, H. C. (London)
 Whiteley, P. (Midlands)
 Woodbridge, R. J. (Bristol)
 Carr, W. (Manchester)
 Butcher, K. W. G. (Manchester)
 Duckett, G. R. (Bristol)
 Finn, S. R. (London)
 Eddowes, D. E. (London)
 Mayne, J. E. O. (London)
 Duligal, E. A. (Transvaal)
 Moon, W. R. (Manchester)
 Brown, A. E. G. (London)
 Collier, C. W. (Trent Valley)
 Jolly, V. G. (Manchester)
 Tate, D. H. (Newcastle)
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 Wilson, A. S. (Manchester)
 Hill, G. V. G. (Trent Valley)
 Campbell, W. H. (London)
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This list was compiled from manual records now transferred to the computer and may contain some inaccuracies. Any member who believes his membership extends for more than thirty-nine years and whose name does not appear on this list, would they please contact me as soon as possible. ■

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Bristol Section

Ladies' Lecture

The Ladies' Lecture for October is the second of the session and was given this year by Sylvia Dannreuther at the Everyman Theatre in Cheltenham where she is Marketing Manager.

The Theatre was built in 1891 to designs by Frank Macham who mass-produced small theatres and opera houses at this time. Few now remain with this probably being the finest. It was renovated and refurbished over a three year period being reopened by The Princess Royal on 8 April 1986.

The Everyman concentrates on its own repertory company which has included Penelope Keith and Frank Windsor prior to their fame. Touring productions are not theatrical, more musical.

In these circumstances the importance and relationship of Director and Designer was discussed and the evening pleasantly concluded with a buffet.

As the Chairman's wife had run off to Holland the vote of thanks was given by the wife of Past Chairman — Chairman Elect Morfydd Saunders.

G. Fowkes ■

Hull Section

Paint additives

The first meeting of the present session was held on Monday, 2 October, 1989 at the Duke of Cumberland Hotel, Cottingham, starting at 7.00pm.

Members and guests heard Mr L Morpeth of BYK Chemie give a talk entitled "Paint Additives, Selecting the Right Tool".

Mr Morpeth introduced his talk by demonstrating qualitatively the dramatic effects of small additions of dispersants to aqueous and solvent-based pigment dispersions. He referred to the "0.5% syndrome" in which an additive would stand or fall on its ability to function successfully at this level and suggested a more thoughtful and systematic approach was required. Defining an additive as a component constituting less than 1% of the formula, he continued with his theme of dispersing/wetting agents.

In aqueous systems, dispersing and wetting agents would be considered separately but in solvent systems, the two were usually combined in one product. Such additives were divided into anionic, cationic and what he termed electroneutral types. Panels

demonstrating how correctly selected additives had ensured proper wetting, resulting in vastly increased gloss were passed around. Dispersants were probably best thought of in terms of their ability to give either deflocculation or controlled flocculation.

The speaker elaborated on this, listing the consequences of uncontrolled flocculation; reduced gloss, colour strength, opacity etc., the merits of complete dispersion; high gloss, colour strength etc, and finally the advantages of controlled flocculation in terms of flooding, floating and sagging.

He went on to demonstrate by way of samples and films, soft and hard sedimentation resulting from controlled flocculation and complete dispersion respectively and the antisagging effect of controlled slight flocculation. Examples of the use of wetting agents were given together with the consequences of incorrect choice of wetting agent.

Moving on to silicone additives, Mr Morpeth categorised various types and related molecular weight of dimethyl polysiloxanes to application. High surface activity of the silicones made little contribution to in-can properties but in films, with their resultant large surface areas, the additives came into their own, reducing surface tension to give great improvement in substrate wetting for example.

The chemistry of silicones, particularly of the modified types was touched on, mention being made of the relationship between molecular structure and foaming, heat and hydrolytic stability and permeability through films etc. By plotting surface tension of a coating against percentage addition of silicone additive, prediction of maximum slip properties was possible.

Referring to automotive coatings, the speaker explained in terms of surface tension differences the defects known as ghosting and overspray incompatibility and the means to avoid such problems. The use of additives to reduce surface tension and ensure wetting of problem substrates was explained and the maintenance of intercoat adhesion was assured provided the additive had the correct molecular structure.

Mr Morpeth finally dealt with the subject of defoamers. Foam was a problem during production, filling and application of paints and foam could reduce efficiency of pigment dispersion. After touching on the theory of foam production and control, the significance of "wet" and "dry" foams and the importance of spreading coefficient, Mr Morpeth mentioned some products available in the BYK range. Some recent products based on crosslinked

polyurea had particularly long lasting qualities, he said which was essential when considering paint application. The foregoing remarks applied mainly to foaming in water based systems. With solvent systems the aim was to achieve a balance between incompatibility and the avoidance of surface defects.

At the conclusion of the talk, the audience posed a number of questions concerning competition for surfactant, predictability of additive performance in different systems, additive specificity, relation between dispersants and dispersion stabilisers and testing. The meeting closed with a vote of thanks to the speaker proposed by the Chairman Mr B. J. R. Mayes and enthusiastically endorsed by the audience.

D. Robinson ■

Manchester Section

Waxes

On Monday, 6 November 1989, a paper entitled "The Role of Waxes in Surface Coatings" was presented to the Manchester section by Mr Karel Jansen of G. M. Langer and Co. K.G. The meeting was held at the Mechanics Institute, Manchester, and was attended by 41 members and guests, the paper being preceded by a buffet, courtesy of Capricorn Chemicals Ltd.

Waxes can be divided into two big groups, natural waxes, and synthetic waxes, the different materials in each group being briefly outlined. Waxes are hydrocarbons with an intermediate molecular weight, below a MW of 1,500 they are classified as oils, between 1,500 and 4,000 MW they are waxes, and those with a MW above 4,000 are plastics or resins.

There are two theories to describe the mechanism by which waxes work, the ball bearing theory, and the surface floatation theory. In practice, a combination of both is probably true, with the ball bearing mechanism predominating in inks, and the floatation mechanism in coatings, due to a film thickness effect.

There are four methods of incorporating waxes into a system:

- ▷ Melt
- ▷ Dispersed
- ▷ Emulsified
- ▷ Micronised

the advantages and disadvantages of each being outlined.

The surface energy of PTFE is very low, and the reasoning behind this was explained. The incorporation of PTFE into waxes can therefore be advantageous, these advantages and the methods used to manufacture PTFE waxes, being described in detail.

The lecturer concluded his paper by outlining the effect on surface coatings of incorporating waxes. Silicas are the most effective for flattening, but waxes give much better all round surface properties, and optimum results are usually obtained using a blend of 1 part wax to 2 parts silica.

Following the lecture there was a lively question and answer session, and the meeting closed with the vote of thanks given by Brian Clementson.

COSHH

The second printing ink lecture of the session, was held on Monday, 20 November 1989. Although redecoration was not complete, the section were able to return to the usual venue of the Silver Birch, Birchwood Centre, Warrington, for this meeting, and prior to the lecture, those attending, were able to participate of a buffet, which was of the usual very high standard of this venue.

Due to unforeseen circumstances, it was not possible to have the lecture advertised in the original programme, and at relatively short notice, Mr Richard Grey of Varnicoat Ltd, presented a paper entitled "The Impact of COSHH on the Printing Industry".

Mr Grey commenced by outlining his personal background, he is an engineer by profession, and is the director responsible for maintenance and safety at Varnicoat. There are six primary obligations to employees outlined in COSHH, and the effects of ignoring, or only paying lip service to these, were outlined. If the regulations are not implemented properly, the unions, knowing their rights, will call in the factory inspectorate. Knowing that full implementation is required by 1 January 1990, the unions are asking about progress, so full implementation is essential.

It is necessary to carry out an assessment of the whole company, this can be done in-house, or using an outside consultant, but in either case, there is a lot of published information available for reference. The implementation of COSHH requires the compilation, and retention, of a considerable number of records, the types of records required were outlined, and the advantages, implications, and disadvantages of this was explained.

It is necessary to carry out a survey of every chemical and process, every hazard has to be known, the ways hazardous materials are handled have to be studied, and procedures monitored. Evaluating everything will determine what is required, and what the costs will be in implementing the regulations.

It is necessary to know what is in

everything you use. Currently there is a lack of information, both on labels, and on health and safety data sheets, and this extra information will have to be obtained from suppliers. The first aim should be to eliminate hazardous materials, and where this is not possible then control measures, and monitoring have to be implemented.

The requirements regarding monitoring and the recording of hazards were outlined, these could be quiet costly, and the basis of these extra costs were indicated, within the framework of the total implications of COSHH.

Mr Grey concluded his lecture with a general assessment of the hazards in the printing industry. This was followed by an extensive and lively question and answer session, and the session closed with a vote of thanks by Norman Seymour.

M. G. Langdon ■

Newcastle Section

Aircraft topcoats

Thirty six members and guests assembled on 2 November 1989 in St Mary's College, University of Durham, to hear Mr Brian Parrott of Desoto Titanine lecture on "Long life Topcoats for Civilian and Military Aircraft".

Mr Parrott began by reviewing typical paint systems used for both civil and military aircraft. It would appear that the older epoxy and acrylic finishes are seldom used, although most coating systems begin with some form of metal pretreatment followed by an epoxide primer. Polyurethane finishes have been standard for many years, especially for civil aircraft where the resistance to phosphate ester lubricant is essential. Aliphatic urethanes also have much better chalk-resistance, an important requirement for modern jet aircraft flying at high altitudes where UV-radiation is much more intense. Military aircraft do not have the continual daily service use demanded of commercial aircraft, but matt/semi-matt camouflage finishes are more critically affected by chalking, and aliphatic urethanes are preferred — chalking causes camouflage colours to change and aircraft performance suffers due to the rougher skin produced.

Over the years urethanes with improved properties have come into general civil use. They are faster curing (4-8 hours masking time) and are more flexible. During application care is needed to avoid airless spray bubble formation or micro-bubbling of carbon dioxide formed by the isocyanate/atmospheric moisture reaction.

The gloss of polyurethane finishes begins to reduce after 2 years on civil

aircraft and re-painting has been common every 5-6 years. This was acceptable because major overhaul cycles corresponded with this period of time. More recently the stretching of engine and airframe overhaul intervals has brought the cost of painting down-time into focus, if this does not synchronise with overhaul times. The lost earnings of civil aircraft or the non-availability of military types during painting is questioned. Attempts to extend re-paint intervals by applying a clear coat of acrylic-urethane as an extra in the standard system extends chalk-resistance time by 1-2 years but also extends the painting down-time, adds extra coating weight, reduces Skydrol lubricant-resistance and results in noticeable yellowing. The need for a longer-life topcoat was obvious.

Mr Parrott described the work done at Desoto Titanine on the development of new finishes. Fluoropolymers were selected for study, taking the exceptional durability of PVDC/PVF coil coatings (20 years min.) as an indication of potential. The performance specification adopted was very demanding in application flexibility, compatibility with older systems, cure temperature-rate, appearance, gloss retention, health and safety factors and cleanability/repair. The necessity for high gloss retention in excess of 10 years required an accelerated weathering test which gave a reliable indication of long-term natural exposure performance. Fortunately they were able to simulate exposure conditions with a particular QUV-cycle, using UVB 313 lamps, such that 100 hours testing was equivalent to 12 months Florida exposure. Using this method typical results were:

Older hard polyurethane	300 hours	10% gloss
Newer flexible polyurethane	1000 hours	40% gloss
Long-life exptl. coatings	1000 hours	90% gloss

The new long-life coatings are isocyanate-cured fluoropolymers and gloss actually improves slightly with weathering. Results were shown for a series of 14 airline colours in both flexible polyurethanes and fluoropolymer polyurethane. Whereas the former had all lost gloss rapidly after 200 hours, reaching 0-10% after 500 hours, the fluoropolymer type actually improved at first, before dropping to the original 85-90% after 200 hours and staying constant thereafter. Similar performance was demonstrated with matt and low-gloss camouflage colours. In addition to better durability, the fluoropolymer types showed improved application performance with a range of spray equipment and climatic conditions. Notable was the low incidence of micro-

bubbling at 35°C and 87%RH, probably due to better release of carbon dioxide as a result of reduced surface tension. The low surface tension also results in easy cleaning.

Trials were carried out on a Concorde. With this aircraft the very high altitude and speed involved necessitates 18 month re-paints. After 4 months service the same order of performance indicated by the QUV tests was noted, with the fluoropolymers type unaffected and the standard polyurethane noticeably reduced in gloss. Other comparative tests on DC 10's and Tristars are showing the same trends. Tests on military aircraft are in progress.

Mr Parrott concluded by saying that user comments showed that ease of application and application schedules are major selling points. Skydrol-resistance and flexibility are both considered adequate. As a result the system has proved acceptable for commercial operations, although the much higher cost may result in slower acceptance for military aircraft where flying hours are much less.

An extended question time afterwards showed the great interest generated. Interesting points to emerge were the cost of grounding a Boeing 747 for 24 hours (£100,000), the weight of paint used on air-liners (300kg-Tristar) and the relative cost of fluoropolymer finishes (three times that of a typical polyester/isocyanate). After the vote of thanks by the Chairman, Mr D. Neal, a splendid buffet meal was enjoyed by all.

J. Bravery ■

Ontario Section

Quality goals

At its first meeting of the section's year, held on 13 September, 1989, the membership was treated to a very comprehensive account of achieving quality goals by Mr Larry Milner of Gaylord Lithographing of Toronto. Mr Milner occupies the position of Quality Assurance Manager of the company.

In his address to the members, Mr Milner spoke on the various steps his company had undertaken to set the goals for quality improvement which in turn would lead to profit improvement. Some of these steps covered the reduction of spoilage, improving the workplace environment, making the pursuit of excellence a daily habit, response to customers needs, efficient use of time and materials and also reduce process variations while at the same time raise the level of customer satisfaction and expectation.

Investing in quality improvement projects can very often produce a return

on investment which is very high. The approach to quality management has to be looked at as a business issue and not just a technical issue. Lip service is paid to the idea of quality performance, whereas a total commitment to improve quality is usually missing.

Managing quality has three essential features, planning of quality goods, control of quality and improvement of same. The quality audit determines that these essentials stay on track.

The planning process which helps to define the quality goals were outlined as follows: material, equipment, people methods and environment.

Mr Milner stated that, at his Company, quality is now a business issue. Company leadership has established policy and specific goals for quality improvement. Responsibility for meeting these goals has been given to the department heads, and not just the quality manager. The company leadership is reflected in the provision of funds for such items as training courses and seminars, purchasing of testing equipment, membership in graphic arts organizations, the purchase of new equipment and repair and maintenance work.

Quality improvement enhances product saleability and operating profit. Quality is the result of doing the right things right and a quality product that has fitness for use. Mr Milner quoted the oft heard old saw "Quality is never too expensive. It is always cheaper to do it right". A much ignored truism.

Mr Milner concluded his address by emphasizing that his company's new approach to quality is less inspection and more attention to prevention of conditions which cause errors and defects. A quality improvement programme is an initiative that encourages everyone to contribute their best efforts to an organization.

J. J. Glynn ■

Scottish Section

OCCA membership

Mr Chris Pacey-Day, the General Secretary, attended a lecture on the 19 September at the Hospitality Inn, Glasgow, when he spoke to members and guests on the benefits of membership of OCCA. He outlined the various features of membership and spoke of the Association's role within the industry. He also spoke of the success of the Journal.

Following this interesting talk a quiz was held, organised by Mr John Dingwall.

H. Jess ■

Trent Valley Branch

Iron oxides

The first meeting of the new season was held at the British Rail Technical Centre on Thursday 19 October, where 40 attendees heard a joint presentation given by Mr Mark Pratt of Harcros Chemicals and Mr Alan Bowden of Troyfell.

Mark Pratt described the historical method of synthetic iron oxide pigment manufacture and outlined the recent changes and advances made by Deanox.

Although the raw materials used in manufacture, namely scrap steel, ferrous sulphate (from the titanium dioxide industry) and caustic are still readily available, the trend of the automotive industry towards using galvanized steel was seen as a future problem in the quality of scrap steel supply.

The many different industries where synthetic iron oxides found applications were described by Mr Pratt with relative consumption given as:

Construction	60-65%
Paints and Inks	25%
Others including foodstuffs	10-15%

Of these markets, construction was seen as offering the largest growth opportunity especially the increase in popularity of coloured block paving.

The second half of the presentation was by Alan Bowden of Troyfell who gave a lecture entitled "Aqueous Dispersions for the Construction Industry". In his talk Mr Bowden outlined the advantages of using synthetic iron oxides in aqueous dispersion form in the manufacture of coloured "concrete" products. The iron oxides are made into five individual aqueous "tinters" from which a whole range of colours can be produced simply by adjusting the volumes of each tinter pumped into the batch of concrete. The benefits of this method to the concrete industry, compared to the supply of dry pigment were stated as:

- ▷ reduced stock
- ▷ more efficient labour
- ▷ faster colour matching
- ▷ cleaner process

A question and answer session followed both papers and a vote of thanks was proposed by Terry Lloyd of Hawleys. A buffet, enjoyed by all present, was kindly provided by Harcros Chemicals.

R. M. Brown ■

Noise management

An audience of twenty members and guests enjoyed a very interesting talk by Peter Wilson on a subject of topical interest.

New regulations regarding Noise Management and Control were published two weeks ago, and become law on the 1st January 1990, and have an impact in the majority of work places throughout Britain and Europe.

Peter Wilson is a partner in the Industrial Noise and Vibration Centre an organisation which has been in being for over twenty five years, and therefore, had a wealth of experience and examples to draw upon in preparing his talk. He concentrated on the implication of the new regulations, and the means by which management can respond to the Health and Safety implications of them.

Time did not permit a detailed examination of all the actions necessary, but he covered in an interesting and informative style the most important areas of immediate action.

With the help of sound recordings he was able to explain what noise was, its energy levels, illustrate the damage extensive noise can do, and explain noise control techniques.

By defining the first action level 85 dB(A), and the second action level at 90 dB(A), given in the regulations, he explained the methods of protection afforded by hearing protection equipment, but at all times concentrated and stressed that noise reduction must be the first priority of management by analysing its source, and understanding it, rather than just relying on the often selected solution of enclosure.

The audience was left in no doubt that he was a man on top of his subject, who had created a very interesting talk, and a generous vote of thanks was forwarded by Mr N. Venn.

D. J. Grantham

West Riding Section

Powder coatings and the development of new additives

The 1989-90 session continued at the Roundhay Mansion Hotel, Leeds on the 17 October with the second lecture given the above title. Richard Harrison of Henkel Nopco addressed an audience of some 40 including more youngsters and ladies than usual. The audience were treated to a well balanced lecture detailing the history-development of powder coatings before moving on to the subject of Henkel Nopco flow additives.

The history of powder coatings was discussed including the differing binder types and their markets. The trends past, present and future predictions were shown for each type. Growth has been shown throughout Western Europe and by 1996 it is expected to reach some 18-20% of the total industrial market.

Following a discussion of the 5 E's economy, excellence of finish efficiency, energy and ecology (of increasing importance) Richard went on to discuss the manufacture of powder coatings. Included were primary extrusion, cooling, grinding and classifying, collection and sieving. The developments of production by spray drying presently going on in the USA were also mentioned.

The application, number of coats and stoving system were covered in some detail before Richard moved on to the subject of flow additives. The benefits of additives in terms of the effects on glass transition temperature, melt viscosity and improvements in melting and decoration were detailed.

The result of tests using Henkel Nopeos Perenol F3 and F40 in such powder coatings were shown and the companies further interest in developing 100% additives emphasized.

A question session was followed by a vote of thanks proposed by Steve Birkett and endorsed by the audience. An excellent buffet and bar was provided, courtesy of Henkel Nopeo.

S. Birkett

OCCA News

Trent Valley Branch

5-A-Side OCCA Competition

The second Trent Valley OCCA 5-a-side soccer tournament was held at the Ramerena, Derby on Friday, 6 October. A total of 12 teams including the holders, Joseph Mason, competed for the "Perfectos Trophy". The competition was based on two leagues of six teams with the top two teams from each league meeting in a semi-final knockout. The final was then played over eight hectic minutes to decide the 1989 champions.

After a keenly fought competition the eventual winners, beating Mebon B team in the final by a convincing 3-0 margin, were Hawleys A Team. The competitors and spectators then retired to the bar where an excellent buffet, arranged by Jill Dibble of Masons, was provided. The Perfectos trophy and winners medals were presented to the Hawleys team and the runners up from Mebon received commemorative pens.

A full list of results is given in the tables below.

R. M. Brown

Trent Valley 5-A-Side Results

League 1

	W	D	L	F	A	Pts
Hawleys A	3	2	0	7	0	8
Mebon B	3	1	1	6	1	7
Masons B	2	3	0	4	0	7
Postans Paints	2	1	2	3	3	5
Hopton Rangers	0	2	3	2	8	2
Odd Sods	0	1	4	3	13	1

League 2

	W	D	L	F	A	Pts
Hawleys GI	3	0	2	5	2	6
Mebon C	3	0	2	5	3	6
Masons A	2	2	1	4	4	6
Thermoset	2	1	2	3	4	5
Mebon A	2	0	3	4	4	4
Perfectos	1	1	3	3	7	3

Semi-Finals

- 1) Hawleys A 1 - 0 Mebon C
- 2) Hawleys GI 1 - 1 Mebon B
Mebon won 2 - 1 on penalties

Final

Hawleys A 3 - 0 Mebon B

Scottish Section

Ladies' Evening

There was a large gathering of members and guests at the ladies' evening held on the 8 September at the Hospitality Inn, Glasgow.

The evening was split into two sections. To launch the evening Dr Susan Beach gave a talk on pedigree sheep and the production of Knitwear in natural colours from their wool. Dr. Beach rears her own sheep and also used wool from many other breeds obtained from elsewhere. Various samples of wool were shown and the differences in texture and feel explained. There was also a short demonstration of spinning.

The second half of the evening was a whisky nosing contest sponsored by Wm. Grant and Sons. Here, members and guests were invited to identify six different whiskies. Some found this more difficult than others. The eventual winner, after a tie break, was Mr Jim Harte who received an appropriate prize.

Mr Howard Jess proposed the vote of

thanks to all involved in producing an enjoyable evening.

H. Jess ■

Fiftieth Anniversary Newcastle Section OCCA

On 17 February, 1942, the Newcastle Section of the Oil & Colour Chemists' Association met for the first time. The section are planning that a "History" be produced and various functions will be held to commemorate this occasion, including a Grand Re-union Dinner for past and present members of the section. Would any members of other sections who would like to be kept informed or who feel they can offer a contribution towards the "History" please contact Mr L. Morpeth, 103 Hallbridge Gardens, Upholland, Lancs., England WN8 0EP. Tel: 0695 623575.

FEBRUARY JOCCA: SURFEX 90 PREVIEW

New members


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

Ordinary members

- Antrim, C. J. (*Thames Valley*)
- Coates, P. (*Midland-Trent Valley Branch*)
- Drummond, C. S. (*Manchester*)
- Falder, J. S. BSc (*Manchester*)
- Ghous, G., MSc, PhD (*General Overseas - Pakistan*)
- Plonka, J. M. (*West Riding*)
- Long, M. D. (*Bristol*)
- Tan, C. H., BSc (*General Overseas - Malaysia*)
- Watson, P. J. H. (*Newcastle*) ■

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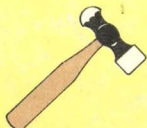
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