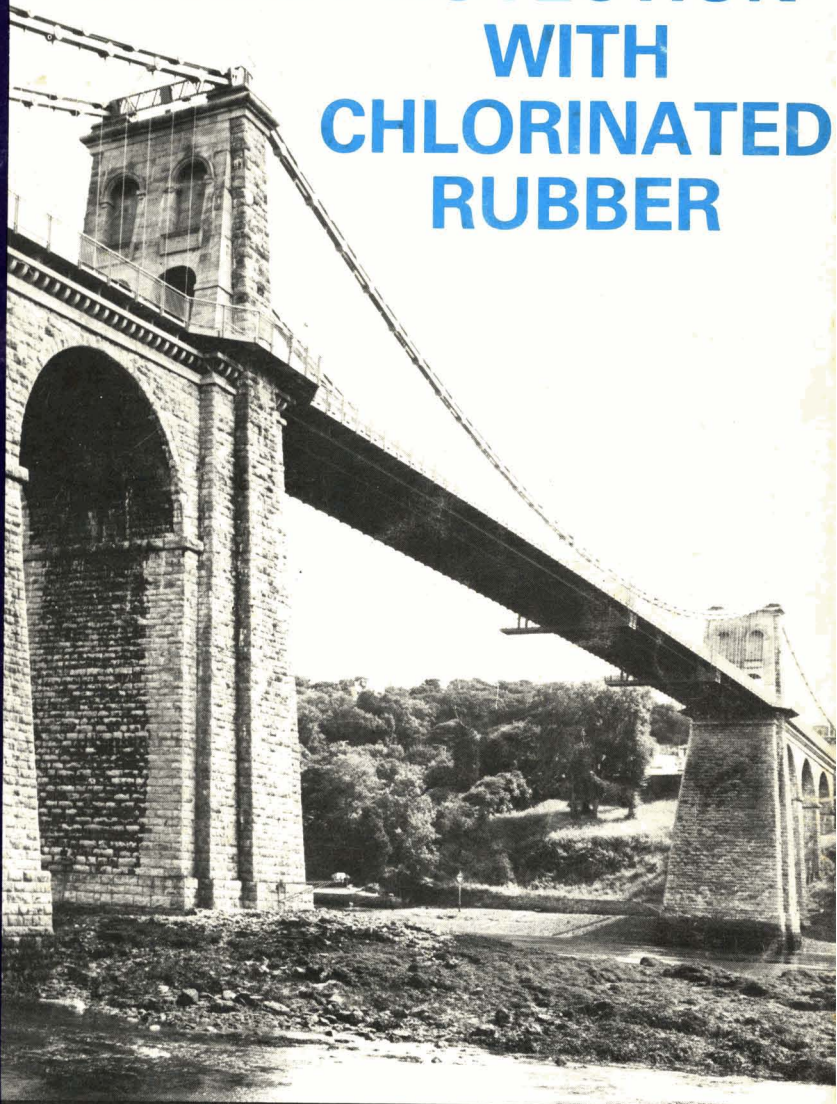




**J
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STEEL PROTECTION WITH CHLORINATED RUBBER



Menai Bridge, Anglesey

ALSO IN THIS ISSUE:

- Nacreous pigments
- Thioxanthenes photochemistry
- Antifouling efficiency using scanning electron microscopy



OIL & COLOUR CHEMISTS' ASSOCIATION

SURFEX 88

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

**HARROGATE INTERNATIONAL
EXHIBITION CENTRE
YORKSHIRE, ENGLAND**

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09.00 - 17.30 hrs**

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

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SURFEX

SURFEX 15-16 June 1988
88
Harrogate Conference Centre

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SURFEX 88

JOURNAL of the OIL AND COLOUR CHEMISTS' ASSOCIATION

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Front Cover Photo courtesy of ICI Chemicals and Polymers Group



E. Merck

Nacreous pigments, p329

OIL AND COLOUR CHEMISTS' ASSOCIATION
Priory House, 967 Harrow Road, Wembley, Middlesex, HA0 2SF England

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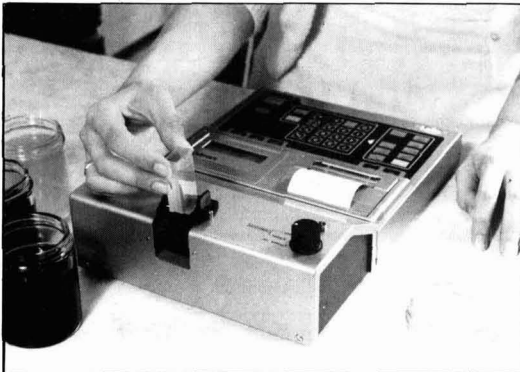
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OCTOBER

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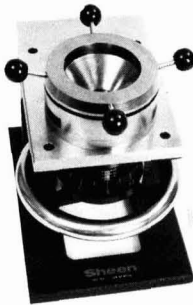
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Rohm and Haas increase European Emulsion Output

Rohm and Haas has announced an increase in its manned capacity at its emulsion plants at Lauterbourg, France, and Jarrow, UK. Also, a new emulsion reactor will be installed in its Landskrona, Sweden, plant in 1988. These steps will provide 25,000 MT annually of additional capacity, bringing Rohm and Haas emulsion capacity at its five European Plants to 120,000 MT annually. Commenting on the expansion programme, Mr Frank Robertson, Director of PRM Business in Europe, stated that the additional capacity reflects Rohm and Haas confidence for the continued growth of its acrylic latexes.

Crown acquires Macpherson Polymers' print finishes

Crown Industrial Paints has acquired Macpherson Polymers' print finishes strengthening its position as UK market leader and establishing it as one of the leading suppliers of radiation cured coatings in the world. The acquisition includes the paper finishing business held by Macpherson Polymers in the United Kingdom, Europe and Far East. John Asher, Managing Director of Crown Industrial Paints, comments: "This move underlines Crown's intention to develop its interests in the rapidly expanding UV curing market. The company is recognised as a leader in innovation and technology and this latest step puts it on the world map in print finishing."

Berger shows faster profitable growth

Increasing links between Berger Britain's decorative companies, Cuprinol, PGW and Berger Decorative Paints are generating greater profitability and improved market positions according to Bill Collins, Chief Executive of Berger Britain on summing up for his half year performance review. Cuprinol, market leader for woodcare products, has recorded sales already 21% above the record level achieved in 1986. Sales of Cuprinol's solvent preserver have continued to increase with also a massive growth in the water-based preserver market of Timbercare. Berger Decorative Paints has also continued to increase its contribution to Group performance in a half-year which has seen the opening of a further 16 Brolac Decorator Centres, bringing the national total to over 150. Both Magicote and Colorizer brands have continued to perform satisfactorily, while Berger has succeeded in further extending its growth with own-brands or retail paint. Much of the continued success for Berger Britain, which underwent major reorganisation three years ago, is attributed to increasing inter-company co-

operation. Typical examples which have already benefitted all companies in the group have been the development of co-ordinated purchasing and the increasing use of all sites within the group to provide extra production capacity for member companies.

Whittaker acquire Polychimie

The Whittaker Corporation of Los Angeles (USA) has acquired from Group Safic Alcan (France) its industrial manufacturing subsidiary Polychimie S.A. located near Orleans (France). The Polychimie acquisition is the Group's first venture into the European speciality chemicals market. Whittaker (turnover \$500m) is a diversified company with principal business activities in North America. Polychimie has expertise in the chemistry of polyurethanes for adhesives and in the technology of formulating wax based release agents and wax compounds for the paint and printing ink industries.

Th. Goldschmidt marketing Phazer Technologies

Phazer Technologies Ltd has signed a consultancy agreement with Th. Goldschmidt Ltd to market within the UK radiation curing silicone based release coatings for paper and film. Phazer Technologies will also provide technical service to Goldschmidt customers under the agreement. Phazer Technologies, formed in May 1986, is headed by polymer chemists Peter Greenway and Tom Alexander.

BSI/ISO approval for Allied Colloids

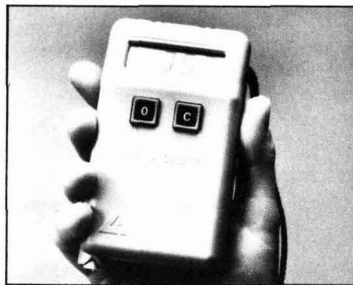
Allied Colloids Ltd have registered with BS 5750 (part 1) 1987 and ISO 9001 - 1987. The double recognition of the company's quality control of their products covers the whole range of speciality chemicals manufactured at Allied Colloids' Bradford headquarters.

Malvern Instruments

The telephone and facsimile numbers of Malvern Instruments Ltd of Worcester have changed to: Malvern 892456 (10 lines), Malvern 892789. The STD code for Malvern, currently 06845, will change to 0684.

Gotec moves

Gotec, manufacturers of spillage absorbents, has moved to Boulton Road, Pin Green, Stevenage, Herts SG1 4QL.



List Mono Check

hand held instrument switches itself on automatically when the built-in probe is applied to the surface under test, and switches itself off again shortly after the last reading has been taken. This allows for one-handed checking of the coating thicknesses on components whilst leaving the other hand free to handle the components. There is a Mono-Check gauge for measuring the thickness of non-magnetic layers on ferrous substrates, and another model for measuring non-metallic and non-conductive layers on non-ferrous substrates.

Reader Enquiry Service No. 20

New solvent

BP Chemicals of Hull has developed *Ethoxy propoxypropanol (EDP)* as the latest addition to its existing range of propylene glycol ether solvents. EDP is manufactured to a consistently high quality by the reaction between ethanol and propylene oxide. It is a high flash, low odour, low toxicity solvent and as such is useful in applications where strong solvents of very low volatility are required. It can function as a high-boiling active solvent in coatings, as a coupling agent for aqueous/organic mixtures, as a carrier solvent, or as a degreaser.

Reader Enquiry Service No. 21

New 2-pack anti crater product

A new ancillary product has been added to the 2-pack system from PPG of Birmingham. Cratering, due to silicone contamination in the workshop can completely ruin a

Anti crater additive



products

New coating thickness gauge

Wymark Technical Products Ltd of Cheltenham has available the *LIST Mono-Check* electronic thickness gauge. This

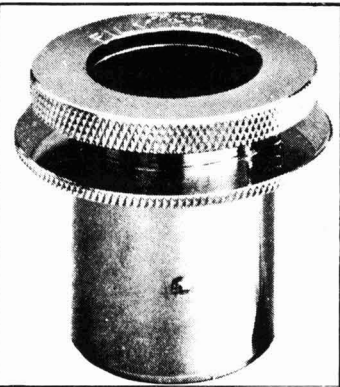
job. Now, with the addition of 10-20 ml of PPG's Anti-Crater Additive, A236 in the acrylic colour or clear lacquer, the problem can be overcome, eliminating the costly exercise of flattening and re-spraying.
Reader Enquiry Service No. 22

Trial kit for silicone additives

Dow Corning has announced the introduction of a new trial kit for its range of silicone additives for paints, inks and resins. The kit is available free of charge from authorised Dow Corning distributors (UK, K & K Greef) and contains 12 of the most popular silicone additives including five new products. A Selection Guide is included so a formulator simply checks the improvement he wishes to make - or the effect he wishes to create - and locates the appropriate Dow Corning additive. Instructions for use are included so trials can be conducted immediately using the sample provided.
Reader Enquiry Service No. 23

Pfund wet film thickness gauge

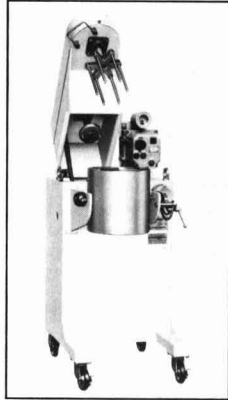
Sheen Instruments of Teddington has available the *Pfund wet film thickness gauge* for use in the laboratory and also on site. Conforming to ASTM D1212, the instrument consists of a spherical convex surface which is forced through the wet paint layer. An over-sized circular paint spot is formed on the glass lens, corresponding to the sum of the thickness of both the original undisturbed paint film and the displaced paint film that wets the glass. A simple 1:1 ratio has been assumed between these two variable thicknesses and used to construct the conversion table which is supplied with the instrument. The table will indicate wet film paint thickness and coverage obtained per gallon of paint.
Reader Enquiry Service No. 24



Pfund wet film thickness gauge

New wet pulverizer

Hosokawa of Shoeburyness, Essex has introduced a new wet pulverizer, called the *Aquamizer*. The new mill is designed for the reduction of hard materials into



Hosokawa wet pulverizer

particles ranging in size from several microns to less than one micron. The *Aquamizer* uses a newly developed agitating pin-type rotor. This has a vertical shaft and the pins operate in a grinding medium of 3mm diameter balls. These balls can be of different materials including stainless steel, tempered steel or ceramic to provide the optimum grinding medium for the material to be pulverized. Among the many advantages claims *Hosokawa MikroPul*, is increased wear resistance and the production of a higher purity product than is possible with conventional ball mills. In addition, material replacement and cleaning of the balls between batches is speedy as the pulverizing tank and agitating rotor are easily separated. Furthermore, the rotor can be replaced without removing the ball medium from the pulverizing tank. Hard or difficult materials such as calcium carbonate, silica sand, titanium oxide barium, iron, barium sulphate and quartz glass - all can be handled effectively by the *Aquamizer*. Typical final particle size and batch grinding times of 0.8 micron in one hour and 0.54 micron in two hours for quartz glass illustrate the mills high performance. This new batch-type wet pulverizer is available in a range of models with pulverizing tank capacities from 7.9 to 40 litres for experimental work and 50 to 1100 litres for production.
Reader Enquiry Service No. 25

Holiday detectors

Elektro-Physik of Cheshire has available a new range of *Porotest* portable high voltage holiday detectors to test for pin holes and porosity in surface coatings. The new *Porotest* is fully portable and is carried by the operator on a shoulder harness, power being provided by built-in rechargeable batteries. The test voltage is generated in the probe handle to which is attached the test electrode.
Reader Enquiry Service No. 26

meetings

Viscometry

The Department of Trade and Industry's Warren Spring Laboratory is to hold a 2-day training course on viscometry on 10-11 February 1988. Intended for technicians and research workers who use viscometers in their everyday work, the course will include lectures and hands-on experience on a range of instruments available at the Laboratory in Stevenage. Methods of calculating data results will be included, together with viscometer selection and the testing of difficult materials. The fee is £298, plus VAT. For further details contact: Ms P. Madhvi, Warren Spring Laboratory, Gunnels Wood Road, Stevenage, Herts SG1 2BX.

Particulate Courses

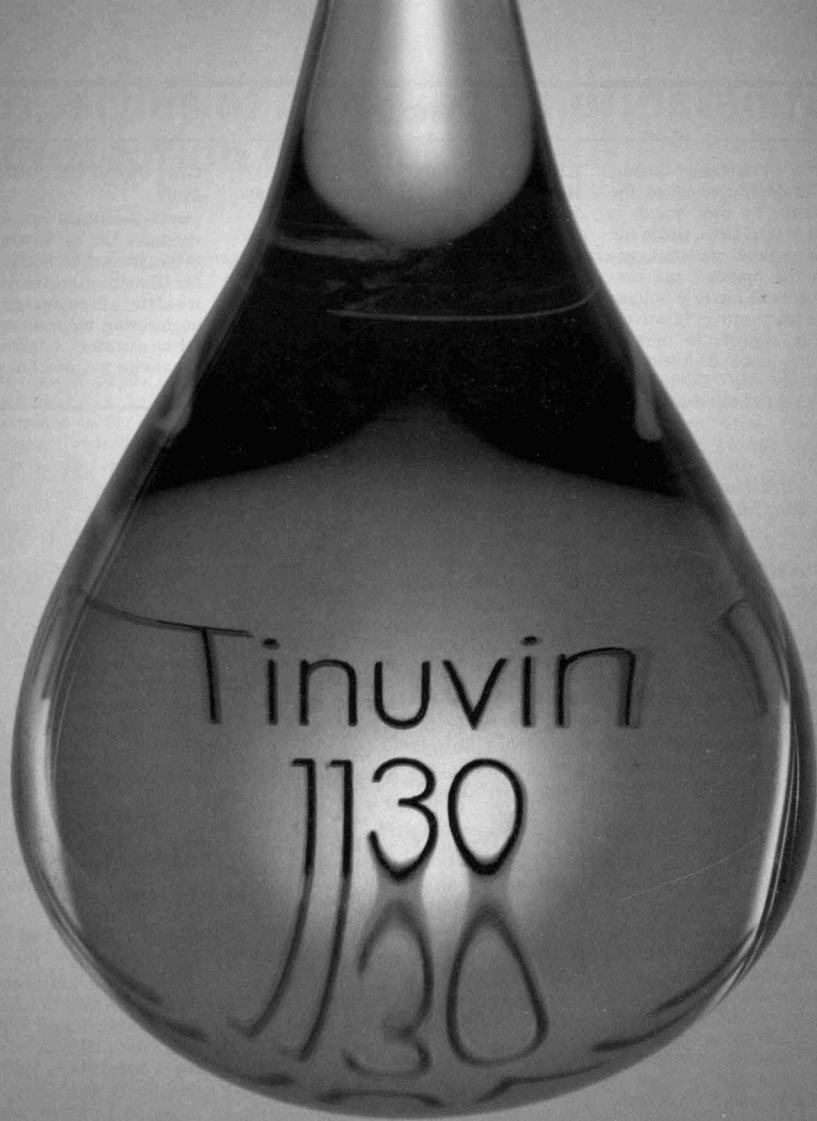
Particle-fluid separation and testing of dry powders are the subjects of three post-experience courses to be held in Amsterdam in the Spring of 1988. The courses are sponsored by the Institution of Chemical Engineers. A 4-day course on Solid-Liquid Separation is to be held from 5-8 April, a 2-day course on Bulk Powder Testing on 11-12 April, and a 3-day course on Two-Phase Separation with Cyclones on 13-15 April. For further information contact: Dr L. Svarovsky, Deputy Chairman, Post-graduate School of Studies in Powder Technology, University of Bradford, Bradford, West Yorkshire BD7 1DP, England.

literature

UK Paint Market Survey

The new Key Note Market Report on Paints and Varnishes comments that with the internationalisation of the paint industry imports will grow at a faster rate than exports. With this, new technology is being introduced by the increasing number of UK subsidiaries of foreign companies, opening up more international markets. ECC countries are the major client and suppliers to the UK market, according to Key Note. West Germany is the dominant partner for paints and allied products with the highest share of trade, replacing Saudi Arabia as the single most important export market. The fall in new building work has caused the decline in the importance of Saudi Arabia.

On the home front, ICI Dulux, the market leader in paints and allied products spends twice as much on advertising as Crown Paints, its nearest rival. Promotional activity is increasing across the board, to counter the growth of own brands, which are slowly eroding the



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market share of many established brands, states the report. In decorative paints, the market accounted for by own brands is already nearly half of total sales, and is still rising. Most leading paint manufacturers now supply both the branded and own brand market in order to increase volume sales. An interesting move however, illustrated by the report, is that of Macpherson Paints, once dedicated to supplying Woolworth with "CoverPlus", which is now seeking to establish its own separate identity with extensive advertising. The report "Paint & Varnishes" at £89 (incl. p+p) is available from Key Note Publishing Ltd, 28-42 Banner Street, London EC1Y 8QE.

EINECS Contact Point (HSD D2), Baynards House, 1 Chepstow Place, Westbourne Grove, London W2 4TF.

people

Croda Resins new Managing Director

Jim Huntley has been appointed Managing Director of Croda Resins. Mr Huntley has extensive knowledge of the resins and allied industries, having been previously employed by Cray Valley Products and the Kalon Group. More recently he ran his own business which had a number of agency agreements for American resin suppliers. A former Chairman of the British Resin Manufacturers' Association and a member of the governing body of the Paint Research Association, Mr Huntley will be based at the company's Belvedere, Kent factory.



Jim Huntley

Exxon Chemicals new marketing manager for solvents

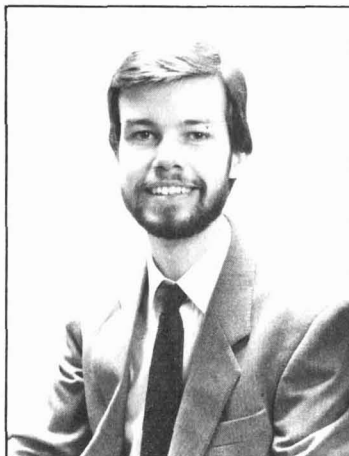
Nick Mockford has been appointed as Exxon's UK Marketing Manager for Performance Fluids and Solvents based at the Company's Head Office in Southampton. Mr Mockford joined the Solvents Division of Exxon Chemical Ltd in 1974 after obtaining a Degree in Applied Economics at the Thames Polytechnic, London. Between 1974 and 1983 he held a number of marketing appointments within Solvents and Chemical Intermediates, before taking up a project management assignment with Exxon Chemical International in Brussels.

Toxide appointments

Mr D. S. Minns, Group Planning Manager, will join the Board of Toxide as Business Development Director.
Dr D. R. Pearce, General Manager, TUKL Pigment Division will become a member of the Toxide Group Executive Committee.

Cray Valley Products add to their staff

David Donaldson has joined Cray Valley Products Ltd as Works Manager at their Stallingborough, South Humberside site. Mr Donaldson comes to Cray Valley with a wealth of experience in chemical engineering and resin manufacture, gained from former employers, I.C.I. plc, Monsanto plc, and Glaxochem plc.



David Donaldson

Allied Colloids Ltd new Board appointment

David Farrar has been appointed to the Board of Allied Colloids Ltd as Research Director. Mr Farrar joined Allied Colloids in January, 1971, as an assistant chemist in the Chemical Services Laboratory and qualified with C.Chem and MRSc after a period of part-time study at Huddersfield Polytechnic. For the last three years he has been Group Research Manager.

bsi news

BSI Committee Meeting: RDB/25 Road Marketing Compounds

At the Committee Meeting held during 23 September, a number of changes were proposed to BS 3262. Of significant interest to members of OCCA will be a change in wording of sections 2.4.3 and 5, to remove the word hydrocarbon. This means that a wider range of resins including those based on Tall Oil Rosin can now be used. This is in line with the Committee's policy to make the standard performance - related rather than formulation based, although at the moment, it is both. In general, there is a move to harmonise standards with those of France and Germany.

The properties of modified chlorinated rubber in the protection of steel

D. Caldwell

ICI Chemicals and Polymers Group, Resins and Surface Coatings Intermediates Business, P.O. Box 13, The Heath, Runcorn, Cheshire WA7 4QF, UK.

Summary

Chlorinated rubber-based paints are accepted as affording excellent protection to steelwork. The benefits that can be obtained from blends of chlorinated rubber with oil-based media as binders for primers and primer/undercoats on blast-cleaned steel are demonstrated. These include rapid build-up of hardness, adhesion, impact resistance, with good salt spray performance as shown by laboratory tests. Exterior exposure testing has concentrated on the evaluations of build-up systems of 1-5 or 6 paint coats applied to specially constructed steel trapezoidal box structures designed to simulate conditions on bridge structures. These tests show that after 6½ years exposure at Teeside UK, good protection has been achieved from as little as 2 or 3 coat systems.

The use of epoxy ester as modifying resin afforded better performance than an alkyd modification. In the latter case zinc chromate with zinc phosphate as anticorrosive offered some boost in performance over zinc phosphate alone, but this was not shown where epoxy ester was used. Good results were noted over a PVB/phenolic blast primer.

These blends offer an ideal combination of properties for new steel protection and also for maintenance painting.

Introduction

Chlorinated rubber based paints are accepted as giving excellent protection to steelwork such as chemical plant, storage tanks, bridges and shipping. Their ease of application, excellent barrier properties, chemical inertness, long life, as well as ease of subsequent maintenance are all recognised as important benefits. Specific painting practices can demand additional properties from paints. Offsite painting and the painting of rust contaminated or previously painted surfaces are instances where the properties required can be obtained by using binders comprising chlorinated rubber modified with other resins. This paper concentrates on the properties that can be achieved by blending chlorinated rubber with oil based media especially in primers and primer/undercoats for use on blast cleaned steel as shown by laboratory testing but with a particular emphasis on long-term exterior durability.

Offsite painting

It has become increasingly popular to apply part of a paint system to steel prior to erection. This technique permits paint to be applied in the factory where drying conditions can be controlled and contamination between coats minimised. Thus ensuring that all parts of the structure, particularly those which become inaccessible after erection, have a sound paint system. Some damage during transportation and erection is inevitable, so the site application will comprise touch-up of the damaged areas followed by the remaining coats of the system.

For a paint system to be used in this way, there are three

basic requirements:

- (1) The paint must dry quickly to facilitate rapid overcoating – essential if acceptable throughput of steel is to be achieved.
- (2) Maximum film toughness must be built up rapidly to permit easy handling without damage.
- (3) The paint must be overcoatable for periods ranging from a few hours to several years, with good intercoat adhesion.

A conventional or pure chlorinated rubber system, i.e. one which is plasticised with a chlorinated paraffin or another inert plasticiser, because it dries by solvent evaporation certainly satisfies requirements 1 and 3. Although a more rapid build up of hardness/toughness may be desirable in some instances, evidence shows that high build paints are perfectly suitable for many offsite painting applications, e.g. they have been specified and very successfully used with new chemical plant construction.

They have also found favour in the offsite painting of motorway pedestrian bridges and overhead gantries, although in this instance, lifting eyes were fitted to facilitate handling.

Some specifiers, such as the UK Department of Transport, who have responsibility for bridges on major highways, have been of the opinion that the traditional chlorinated rubber film takes too long to build up ultimate hardness.

To overcome this criticism two modifications were developed incorporating alkyd or epoxy ester as the co-resin with chlorinated rubber and both types will be discussed.

Blends of chlorinated rubber with oxidising media

It is well known that if paints based on oxidising media are overcoated with coatings which contain strong solvents then rivelling can occur if the oxidising resin has only partly cured. This effect may be noted when overcoating alkyds, vinylated alkyds, epoxy esters and blends with non-convertible resins such as chlorinated rubber or acrylics.

In the case of chlorinated rubber blends this effect is also dependent on the choice and level of oxidising resin and of course the drying time before overcoating. In general a high chlorinated rubber content and reduced oil length of co-resin will be beneficial. Also for fast dry there will be a leaning to the shorter oil alkyds but with due regard to compatibility of the final binder which is normally reduced with shorter oil length.

A ratio of 'Alloprene' chlorinated rubber alkyd or epoxy ester of 2/1 on solids has been found beneficial in obtaining

good overcoating and the fast attainment of mechanical properties. With this level of chlorinated rubber a small amount of additional plasticiser will be needed e.g. chlorinated paraffin to achieve the required film flexibility. This can also help with film compatibility.

For alkyd modification a ratio of chlorinated rubber/alkyd/chlorinated paraffin = 20/10/5 by weight is close to optimum. 'Alloprene' R5 chlorinated rubber, 'Plastokyd' 601X, short oil rosin modified DCO alkyd (Croda Resins Ltd UK) which is suited for paints for offsite application and 'Cereclor' 42 chlorinated paraffin were used. Longer oil length drying oil modified alkyds at the same ratio may be preferred for maintenance work.

For epoxy ester modification a ratio of chlorinated rubber/epoxy ester/chlorinated paraffin = 53/27/20 is close to optimum. In our work 'Alloprene' R10 chlorinated rubber, 'Synolac' 463X a DCO ester, (Cray Valley Products), and 'Cereclor' 42 chlorinated paraffin were used.

Laboratory testing

The properties obtained by blending can be demonstrated by laboratory testing. By this means it can be shown how the requirements for offsite painting can be achieved by modifications with alkyd or epoxy ester whilst maintaining substrate protection. The tests involved mechanical and accelerated testing of pigmented compositions using zinc phosphate alone and a blend of zinc phosphate/zinc chromate as anti-corrosive which was fashionable at the commencement of the work.

Scratch hardness

Substrate - pyrene mild steel
System - 1 x 60 µm dry film thickness of primer
Tested to BS3900: Part E2, 1970

Table 1

Binder*	Load to failure in g after	
	24 HOURS	7 DAYS
CR/CP 70/30	700	1000
CR/Alkyd/CP 20/10/5	1000	2000
CR/Epoxy Ester/CP 53/27/20	1000	2200

* CR = 'Alloprene' chlorinated rubber; CP = 'Cereclor' chlorinated paraffin

The results in Table 1 clearly show the greater hardness that can be achieved by resin blending, of importance in handling of painted steel.

Cross hatch and elcometer adhesion

Substrate - 4 mm steel shot blasted to Swedish Standard Sa 2½

System - 2 x 60 µm film thickness of primer/undercoat (P/UC)

Preparation - Panels dried for seven days at ambient temperature

Testing - Cross hatch to BS3900: Part E6, 1974 (0 - 5 scale, 0 = perfect)

Elcometer pull-off adhesion test

Table 2

Binder*	Cross Hatch	Elcometer
CR/CP 70/30	0	cohesive P/UC
CR/Alkyd/CP 20/10/5	0	cohesive P/UC
CR/Epoxy Ester/CP 53/27/20	1	cohesive P/UC

* CP, CR are defined in Table 1

All systems are showing excellent adhesion characteristics even though thinner first coats would normally be recommended. Similar results have been obtained over 1 and 2 pack PVB blast primers.

Falling ball impact

Substrate - 4 mm steel shot blasted to Swedish Standard Sa 2½

System - 2 x 60 µm film thickness of primer/undercoat

Preparation - Panels dried for seven days at ambient temperature followed by two hours at 0°C

Testing - To BS3900: Part E7, 1974

Table 3

Binder*	Falling Ball Impact
CR/CP 70/30	no loss of adhesion
CR/Alkyd/CP 20/10/5	no loss of adhesion
CR/Epoxy Ester/CP 53/27/20	no loss of adhesion

* CP, CR are defined in Table 1

Under these conditions of test no adhesion loss was noted on steel. These primer/undercoats have also performed satisfactorily over zinc rich epoxy and epoxy iron oxide primers.

Accelerated tests

Substrate - Steel blast cleaned to Swedish Standard Sa 2½

System - 2 x 30 µm primer

Preparation - 24 hours between coats, seven days ageing of final coat before test

Table 4

Binder*	Anti-Corrosive	3000 Hours Salt Spray
CR/CP = 65/35	Zinc Phosphate	8
CR/Alkyd/CP = 20/10/5	Zinc Phosphate	7
CR/Alkyd/CP = 20/10/5	Zinc Phosphate/ Zinc Chromate	10
CR/Epoxy Ester/CP = 53/27/20	Zinc Phosphate	7

* CP, CR are defined in Table 1

Testing - Salt spray to BS3900: Part F4, 1968 assessed on 0-10 scale where 10 = No failure

From Table 4 it can be seen that good results can be achieved even after prolonged testing. The better barrier properties of the chlorinated rubber/chlorinated paraffin binder are shown using zinc phosphate as anti-corrosive. The more active anti-corrosive blend upgrades the alkyd modification. Using a chlorinated rubber/chlorinated paraffin binder in subsequent coats provides a barrier and can give maximum benefit from the total system.

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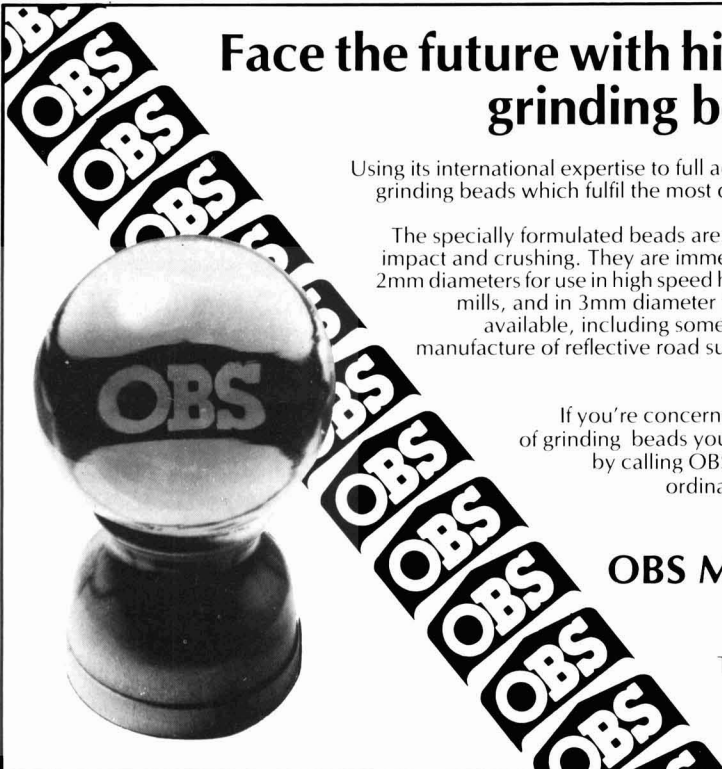


Table 5

Constituents*	Zinc Phosphate/ Zinc Chromate		Zinc Phosphate	
	Alkyd	Epoxy Ester	Alkyd	Epoxy Ester
'Alloprene' R5 (a)	13.8	—	13.9	—
'Alloprene' R10 (a)	—	12.3	—	12.6
'Plastokyd' 601X (b)	13.8	—	13.9	—
'Synolac' 463X (c)	—	10.4	—	10.7
'Cereclor' 42 (d)	3.4	4.6	3.4	4.7
Pure zinc chrome	5.1	5.1	—	—
Zinc phosphate	21.9	21.8	22.1	22.4
'Tioxide' RCR2 (e)	6.4	6.4	7.2	7.3
Yellow iron oxide	—	—	0.5	0.5
Red iron oxide 120Y	0.8	0.8	—	—
'Microtalc' AT1 (f)	—	—	4.2	4.2
Maleic acid	0.4	—	0.4	—
'Thixomen' (g)	1.5	1.5	1.5	1.5
Methyl ethyl ketoxime	0.1	0.1	0.1	0.1
Xylene	24.9	28.8	24.9	28.2
'Solvesso' 100 (h)	7.9	8.3	7.9	8.1
Volume solids %	39.0	38.0	39.0	39.0
PVC %	34.0	34.0	35.0	35.0
Viscosity 10,000 sec ⁻¹ poise	1.5	1.5	1.5	1.5

* (a) 'Alloprene' – chlorinated rubber – ICI, UK.

(b) 'Plastokyd' 601X – short oil rosin DCO alkyd – Croda Resins Ltd, UK.

(c) 'Synolac' 463X – DCO epoxy ester – Cray Valley Products, UK.

(d) 'Cereclor' 42 – chlorinated paraffin – ICI, UK.

(e) 'Tioxide' RCR2 – titanium dioxide – Tioxide Group PLC, UK.

(f) 'Microtalc' AT1 – talc – Norwegian talc A/S, Norway.

(g) 'Thixomen' – modified hydrogenated castor oil – ICI, UK.

(h) 'Solvesso 100 – trimethyl benzene – Esso Petroleum Co.

Overcoating

Primers formulated with a 3/1 ratio of chlorinated rubber/midifying resin in the binder have been shown to overcoat satisfactorily with a high build coating containing aromatic solvents after time intervals varying from two hours to six months drying of the first coat. In contrast there may be time intervals when coatings based on alkyd or epoxy ester alone could show sensitivity to overcoating.

Exterior exposure

The ultimate test for any paint system is its performance in user conditions. Laboratory tests can give an indication of expected performance, but exterior exposure is the real proof. Exposures on panels and trapezoidal box sections have been made, and the paint systems and results obtained are detailed below.

Paint variables and systems

Formulation variables in this exposure series included the following:

In blast primers and primer undercoats.

Binders – CR/Alkyd/CP and CR/Epoxy Ester/CP.

Anti-corrosive pigmentation – Zinc phosphate, zinc

phosphate/zinc chromate.

Typical primer undercoat formulations used in this work are detailed in Table 5. These are for spray applied paints. Blast primers were prepared by adding further solvent to give 1.0 poise viscosity.

The blast primer for one box was a commercial PVB/phenolic. A pure chlorinated rubber based MIO undercoat and finish were used as the final coatings of the system.

The full systems are as follows:

CR based blast primer 25 μ m (15 μ m where PVB used)
 CR based primer/undercoat 3 x 40 μ m (2 x 60 μ m where PVB used as blast primer)
 CR-MIO undercoat 80 μ m
 CR finish 25 μ m
 Dry film thicknesses are given.

Panel exposures

Table 6 details results from two series of exposures at the Widnes Site of ICI PLC Chemicals and Polymers Group (industrial environment), for paint systems on steel blast

Paint and Surface Coatings

Theory and Practice



Edited by R. LAMBOURNE,
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INDCOLLAG (Industrial Colloid
Advisory Group), Department of
Physical Chemistry, University of
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cleaned to Swedish Standard Sa 2½.

Primer System

Two coats = one coat of blast primer plus one coat of primer/undercoat

Four coats = one coat of blast primer plus three coats of primer-undercoat

All paints were airless spray applied.

Gaps in the readings relate to combinations that were not tested.

Table 6

Time on Exposure	7 Years 6½ Years		
Primer System	2 Coats 4 Coats		
Primer Binder	Primer Anti-Corrosive		
CR/Alkyd/CP	ZP	OK	OK
CR/Alkyd/CP	ZP/ZC	—	OK
CR/Epoxy Ester/CP	ZP	OK	OK
CR/Epoxy Ester/CP	ZP/ZC	—	OK

Key

CR = 'Alloprene' chlorinated rubber

CP = 'Cereclor' chlorinated paraffin

ZP = Zinc phosphate

ZC = Zinc chromate

OK = No film breakdown other than minimal chalking

From the long term panel exposure excellent steel protection has been achieved even in coatings of relatively low film build from binders based on CR/alkyd or epoxy ester blends.

Testing on trapezoidal boxes

In the UK the Department of Transport use specially constructed boxes to provide data on paint performance with particular reference to bridge construction. As part of a comprehensive test programme a series of modified CR paint systems were included in tests on trapezoidal boxes and exposed at an industrial situation close by the River Tees in North East England.

Trapezoidal boxes provide a variety of surfaces on which to test paints. Those used for these tests were constructed six feet in length, with a 16" width top plus a one inch downwards facing lip along each six foot edge. The sides taper inwards to give a bottom face of approximately 10" width. The boxes have sealed end plates. They had a final weight of approximately 112 lbs. Side arms permit rolling on a retaining frame thus facilitating examination of all painted surfaces.

Surface preparation

The boxes used for the trials were of steel construction and had weathered without painting for 12 months before use, after which time severe rusting had ensued. Surface preparation before painting was by blasting with G12 grit to achieve a surface corresponding to Swedish Standard C Sa 2½-3. Paints were applied as build up systems from one to five or six coats. Each layer of the build up encircles the whole box and gives a good area for examination of the performance of each part of the build up. One day's drying minimum was allowed between coats. Paint application was

by airless spray using a Graco King machine. The steel temperature varied within the limits 16-21°C with the relative humidity close to 63%.

Exposure at Teeside

Painted boxes were exposed at Teeside in Autumn 1978.

Evaluation

At intervals of time over the test period, evaluations have been made for film breakdown of each build-up and recorded in Table 7, in which data is presented for the three types of surface under investigation. Up to the five year four months evaluation no corrosion breakdown was observed where greater than two paint coats are involved. Here only minimal chalking of the MIO and finish coats was noted. At the six year five month evaluation some corrosion spots are now seen in the three coat build-up. Here only those results where some corrosion failure has occurred at a particular build-up level have therefore been included but omitting the single coat results at the six year five months stage where considerable corrosion has resulted after this long test period. As an aid to clarification of the data in Table 7, Figures 1-2 show coated boxes after six years five months. These were taken after washing the paintwork with water.

Conclusions

Considering the results it can be concluded that:

- (1) In terms of severity of corrosion Box base > Box side > Box top – A result in line with expectations.
- (2) Considering the film build – An increase in film build results in improved performance from one to three coats. The single coat of CR based blast primer showing limited protection, the two coat system giving good protection at three years exposure and three coats at more than six years.
- (3) Comparing the two modifications of 'Alloprene', which were evaluated, the epoxy ester gives better performance than the alkyd but would add to paint costs.
- (4) In alkyd modification, blending of zinc chromate with zinc phosphate offered benefit, whereas in the epoxy ester modification this was not noted.
- (5) On the PVB/phenolic, the epoxy ester modification had the edge at two coats thickness.
- (6) Considering the paint formulation variables in terms of binder and anti-corrosive the following approximate order of performance results.

CR/EE/CP (ZP) > CR/EE/CP (ZP/ZC) > CR/ALKYD/CP (ZP/ZC) > CR/ALKYD/CP (ZP)

Overall comments

Correctly formulated blends of 'Alloprene' with alkyd or epoxy ester offer practical benefits in painting systems. Particularly in terms of:

- Mechanical properties.
- Rapid build-up of hardness.
- Good adhesion to steel.

Figure 1. Test box after 6 years 5 months exposure at Teeside

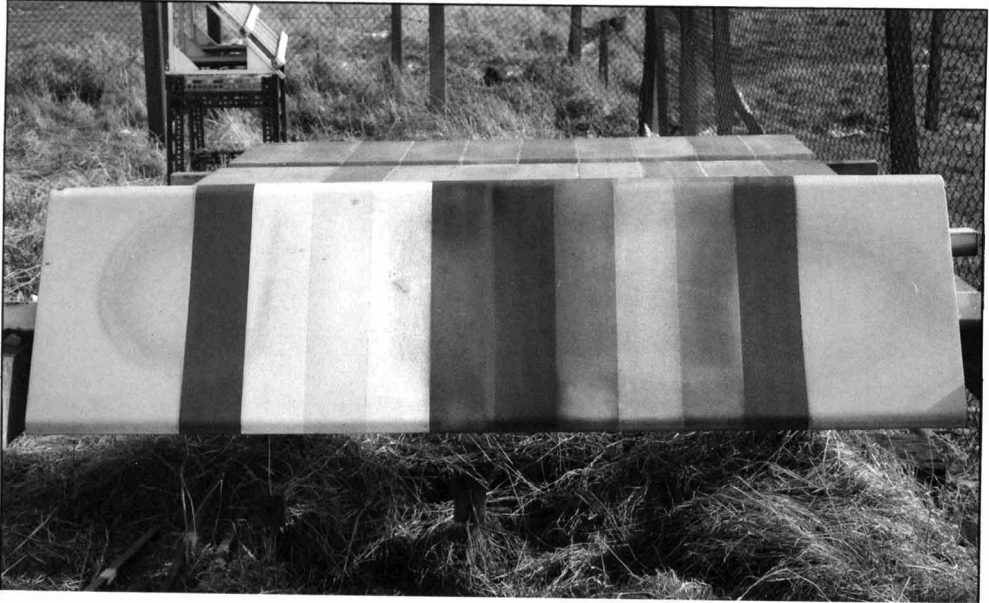
CR/Epoxy Ester/CP Binder for Blast Primer and Primer Undercoat

Zinc Phosphate Anticorrosive



Zinc Phosphate/Zinc Chromate Anticorrosive

Box Top



6	5	4	3	2	1	1	2	3	4	5	6
---	---	---	---	---	---	---	---	---	---	---	---

Total Number of Paint Coats



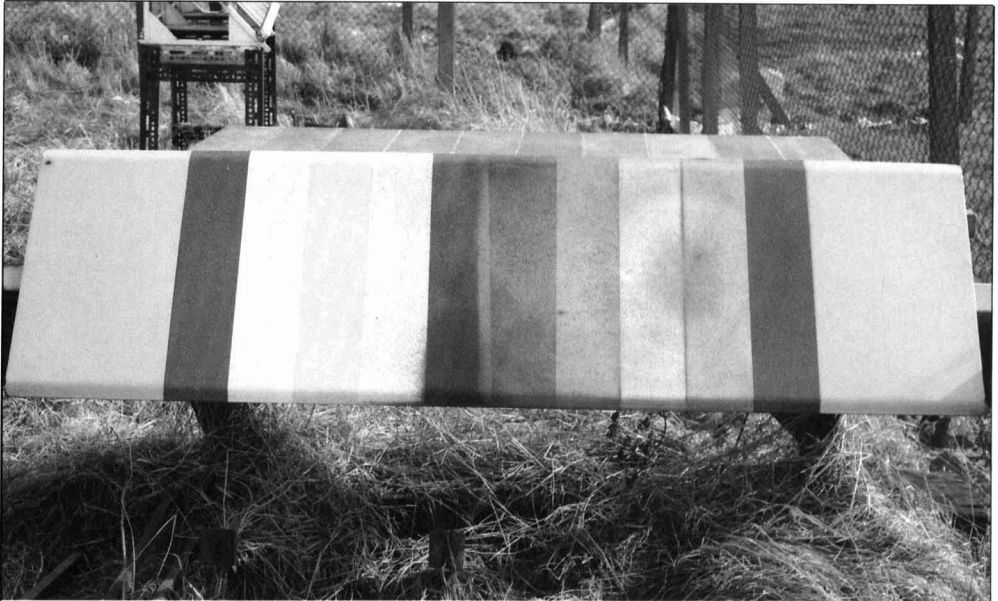
Box base and sides

**Figure 2. Test Box after 6 years 5 months exposure at Teeside
CR/Alkyd/CP Binder for Blast Primer and Primer Undercoat**

**Zinc Phosphate Anticorrosive
Box Top**



Zinc Phosphate/Zinc Chromate Anticorrosive



6	5	4	3	2	1	1	2	3	4	5	6
---	---	---	---	---	---	---	---	---	---	---	---

Total Number of Paint Coats



Box base and sides

Exterior exposure results at Teeside

Blast Primer and Primer Undercoat	9 Months			3 Years			5 Years 4 Months									
	1 Coat			1 Coat			1 Coat									
	Top	Sides	Base	Top	Sides	Base	Top	Sides	Base							
Anti-Corrosive	Top	Sides	Base	Top	Sides	Base	Top	Sides	Base							
Binder	Top	Sides	Base	Top	Sides	Base	Top	Sides	Base							
CR/Alkyd/CP	—	8	4	OK	OK	OK	VFRS	6	0	OK	FRS	FRS				
CR/Alkyd/CP	—	8	6	OK	OK	OK	FRS	MRS	1	1	OK	MRS				
CR/Epoxy Ester/CP	—	OK	OK	OK	OK	FRS	FRS	FRS	MRS	MRS	OK	FRS				
CR/Epoxy Ester/CP	—	9	9	OK	OK	OK	OK	OK	VFRS	5	SRS	FRS				
Blast Primer – PVB/Phenolic																
Primer Undercoat																
Binder	Top	Sides	Base	Top	Sides	Base	Top	Sides	Base	Top	Sides	Base				
Epoxy Ester	—	—	—	OK	OK	OK	—	8	OK	—	VFRS	3	8MD + 8MD + Broken Blisters	OK	FRS	FRS
CR/Alkyd/CP	—	—	—	OK	OK	OK	—	8	OK	—	RS	3	8MD + 8MD + Broken Blisters	OK	MRS	MRS
CR/Epoxy Ester/CP	—	—	—	OK	OK	OK	—	8	OK	—	VFRS	3	8MD + 8MD + Broken Blisters	OK	MRS	MRS
Blast Primer and Primer Undercoat																
2 Coats																
Binder	Top	Sides	Base	Top	Sides	Base	Top	Sides	Base	Top	Sides	Base				
CR/Alkyd/CP	CR/Alkyd/CP	ZP	ZP/ZC	OK	VFRS*	FRS	FRS	FRS	FRS	OK	RS(1) Damage	VFRS				
CR/Alkyd/CP	CR/Alkyd/CP	ZP/ZC	ZP/ZC	FRS	FRS*	MRS	MRS	MRS	FRS	RS(3) Damage	OK	VFRS				
CR/Epoxy Ester/CP	CR/Epoxy Ester/CP	ZP	ZP	OK	RS(1)*	FRS	FRS	FRS	FRS	OK	OK	OK				
CR/Epoxy Ester/CP	CR/Epoxy Ester/CP	ZP/ZC	ZP/ZC	OK	OK*	FRS	FRS	FRS	FRS	OK	OK	OK				
Blast Primer – PVB/Phenolic																
Primer Undercoat																
Binder	Top	Sides	Base	Top	Sides	Base	Top	Sides	Base	Top	Sides	Base				
Epoxy Ester	ZP	ZP	ZP	FRS	OK*	VFRS*	FRS	FRS	FRS*	OK	OK	OK				
CR/Alkyd/CP	ZP	ZP	ZP	VFRS	RS(1)*	FRS*	VFRS	FRS*	FRS*	OK	OK	OK				
CR/Epoxy Ester/CP	ZP	ZP	ZP	OK	OK*	FRS*	FRS*	FRS*	FRS*	OK	OK	VFRS				

Key

CR = 'Alloprene' Chlorinated Rubber
 CP = 'Cerecor' Chlorinated Paraffin
 ZP = Zinc Phosphate
 ZC = Zinc Chromate
 PVB = Polyvinylbutyral
 8MD refers to blistering on the ASTM scale
 RS = Rust Spots (No. in brackets)
 VFRS = Very Few Rust Spots
 FRS = Few Rust Spots
 MRS = Moderate Rust Spotting
 SRS = Severe Rust Spotting
 — = Reading Not Taken
 Corrosion on a 0-10 Scale where 0 = Completely Rusted
 * = Reading Recorded is Better Than at Previous Evaluation - Possible Surface Contamination.

- Good low temperature impact resistance.
- Good recoating characteristics.
- In laboratory immersion tests, a slight fall off in performance may be expected from that given by a full CR system, but systems completed with CR/CP top coatings provide the ultimate barrier against external attack.
- Excellent exterior durability as demonstrated by panel exposure tests in industrial Widnes and especially on trapezoidal box sections at Teeside. After six-and-a-half years good protection had been achieved from two/three coat systems.

The above results demonstrate the benefits that can be obtained and thus indicate why this type of system has found favour for structural steel painting and has found acceptance in the painting of large structures such as the Britton Ferry and Tinsley Viaducts in the UK, as well as pedestrian footbridges and sign gantries on major roads.

Although not part of this current discussion, it is worth

Colouration and colour enhancement of inks by nacreous pigments*

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Synopsis

This paper describes the phenomena known as iridescence and pearlescence derived from mica based pigments. A usage in today's printing ink systems, alone or in combination with other colorants to bring about additional dimensional and aesthetic effects in colour are discussed.

The infinite variety of nacreous colour effects that one sees in nature has been, throughout the ages, of great interest to everyone both to match and to utilise.

Unfortunately, nature does not offer nacreous substances in commercially significant and easily accessible quantities for this purpose. Also when they occur they are mostly not pure or stable enough to satisfy industrial and environmental demands. This is also the case for pigments used in printing inks that are subsequently to be used for foodstuff, packaging and toys.

Accessibility of naturally occurring coloured nacreous substances—to be subsequently converted into pigments—is virtually impracticable.

Take for example the inside of a mussel shell: it exhibits nacreousness (more often referred to as pearlescence); that is lustre and iridescence, when incident light shines upon it. This optical effect (what one sees as pearlescence) arises from the laminar structure of transparent multi-layers of chalk interdispersed with transparent layers of a protein substance (collodion) and the inter-reaction of the incident light at each of the interface boundaries.

If one attempts to mechanically obtain the mussel shell's pearlescent layer in a finely divided form, as is the requirement of an ink pigment, then the pearlescent characteristic will be almost totally destroyed. It is similar to the result obtained when multi-brown coloured crystal sugar is

adding a final comment that 'Alloprene' blends with alkyd, epoxy ester, or oleoresinous media also have benefits in achieving good performance in maintenance situations where rust contaminated steel may form part of the substrate. These modifications also assist in achieving good application properties from paints formulated for brush application which may be more appropriate on this substrate.

Acknowledgements

I would like to thank ICI's Chemicals and Polymers Group for permission to publish this paper, and the Department of Transport, UK, without whose assistance with provision of box sections and use of their Teeside Test Site much of this work would not have been possible.

The names 'Alloprene', 'Cereclor' and 'Thixomen' are trade marks, the property of Imperial Chemical Industries PLC.



M F N S L
 TiO₂ - MICA PLATELETS OF DIFFERENT PARTICLE SIZE DISTRIBUTION
 M: 1 - 15 MICRON (90%)
 F: 5 - 20 MICRON (90%)
 N: 10 - 50 MICRON (90%)
 S: 10 - 130 MICRON (90%)
 L: 40 - 200 MICRON (90%)
 THICKNESS: 0.1 - 0.5 MICRON

Figure 1. Pearlescent mica pigment: Mica/metal oxide.

ground down to a fine powder. The result: a mono coloured very pale yellow powder.

Nacreous substances possess a common feature—they are platelets, some regular, others irregular in shape. An abundantly occurring mineral having platelet form which is very transparent and is almost colourless in this finely divided platelet form can be converted into the laminar structure required of a pearlescent pigment, is—Mica.

Mica has a refractive index of 1.6. Deposition of layers of transparent metal oxides (having higher refractive indices) onto its surface give rise to the pearlescent mica pigments—Iriodin (Figure 1).

As with the mussel shell, Iriodin pearlescent pigments behave towards incident light in several ways: they reflect light and due to their transparency, they transmit light. The light that is transmitted and transverses the pigment platelets does not do so in a straight line, for at each boundary interface of the pigment it is refracted. Likewise

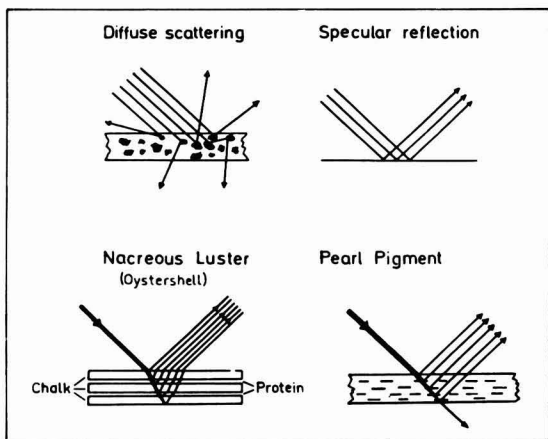


Figure 2. Pearlescent coloration derived from incident light distortion.

for inks, as the light is refracted at each interface of the pigment boundaries so it is refracted between the pigment and ink vehicle.

Thus as the reorientated incident light is reflected back through the ink vehicle one observes the physically distorted emergent light which has the optical appearance of pearlescence and iridescence (Figure 2).

Controlled deposition of transparent titanium dioxide layers ($n_D = 2.5 - 2.7$) onto the mica pigment gives rise to a defined series of colour effects.

The first series are the pearl (silver)—Iriodin 100 series.

The second series consists of interference colours—Iriodin 200 series. Each pigment of this series exhibits two specific colours. One of which is the interference colour which can only be seen by changing the viewing angle. And is created by the transmission and back reflectance of the incident light from the various phase boundaries.

The Iriodin interference pigments are often used in inks, coatings and lacquers to give further colour dimensions e.g. brilliance, depth and "flop" to a colour or an overlacquer. For example a green with a violet "flop" colour.

The next three-series of pigments—Iriodin 300, 400 and 500, contain other metal oxides. These give rise to metallic colours such as golds, greens and bronzes.

Effect of particle size range

The Iriodin mica-based pearlescent pigments consist of minute platelets of irregular surface shape. Their surface dimensions range from 2-150 μm while their thickness is rigidly controlled to be within the range of 0.4-0.5 μm . A further grading of the pigments within the proven particle size ranges of < 15 μm , 5-20 μm , 10-60 μm , 30-150 μm is carried out.

Thus the smaller particle size ranges give good covering power, less gloss and a silk-satin lustre in an ink, whilst the larger particle size ranges give rise to silky lustre, pearly lustre, glitter through to a sparkling lustre—but with

decreasing covering power with increase in particle size.

The range of particle sizes offers yet another dimension, in terms of print finish, when considering the nacreous colour effect and covering power.

Iriodin pearl lustre pigments can be incorporated into almost all types of printing inks vehicles—including those based on water, solvent, modified oil/resins, UV- and EB-curing ink systems.

In most cases the pigment particle size ranges that one can use, will be governed by the following criteria!

1. The screen mesh opening.
2. Cell sizes and shapes.
3. The printing process.

Combination with other colourants and the enhancement of colourants in printing inks

Iriodin pearlescent pigments can be used by themselves as colourants. In these cases one must always remember that they are transparent pigments and that the under colour will play a strong part in the colour observed. For example an ink formulated with a pearl pigment and printed onto a black background will give rise to a silver metallic colour—aluminium.

When Iriodin pearlescent pigments are combined with other transparent dyestuffs or transparent pigments (Note: non-transparent colourants can not be used with pearlescent pigments) an enormously wide range of iridescent and brilliant colours can be obtained. Higher concentrations give better results. In the context of an additive, they can also be used in small amounts to enhance the performance of a dull and lifeless colour, by improving its brilliance and giving it depth—a third dimension.

Mixing

Mixing processes that involve high shear and crushing forces should not be used to mix in pearlescent pigments into an ink or lacquer phase. Pin-mills, sand-mills, ball-mills should be avoided as they will crush the pigment platelets. Triple roll-mills can be used with extreme care.

By far the best method is to gently stir in the pre-wetted pigment (solvent or vehicle), this will give a quick and agglomerate free dispersion.

Effect of ink thickness and pigment orientation

The ultimate and best nacreous effect realisable from pearlescent pigments is when the pigment platelets are orientated planar to the substrate surface. The thicker the ink layer the better the effect. Irregular orientation will give rise to light scattering and thus reduces the nacreous effect.

Inks that have good flow characteristics, such as screen, flexo and gravure give a better chance for the pigments platelets to orientate themselves planar to the printed surface.

Powder printing processes

All the Iriodin pearlescent pigments can be used in the dust-on powder printing processes such as bronzing and

thermographic printing.

Interestingly, for the bronzing process, this aspect enables one to obtain many further colour dimensions for the golds and silvers and, additionally the iridescent interference colours can be utilised in this process.

As mentioned earlier, Iriodin pearlescent pigments function optically by the reflection, transmission and re-emergence of light through them. Thus the choice of the other partner pigments, colourants or the undercolour of the base material (e.g. printed or coloured) and the clarity of the ink medium are important factors to be observed in the understanding of their function in the final ink colour effect. This can be contrasted with a theatre stage designer who completes his set, by careful stage-lighting with the stage back-drop, to obtain unique and enhancing colour effects.

Conclusion

Iriodin pearlescent pigments are nacreous pigments with an

inorganic base that behave almost like a living organism. They bring life into otherwise dull colours. They are environmentally harmless, inert to pH variations and have a temperature stability up to 850°C.

The realisation of their function opens-up to the designer, the colourists, the ink manufacturer and the printer, a completely new dimension and concept of colours and effects only achievable by printing with and in combination with nacreous pigments.

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Photopolymerisation and photochemistry of methyl, propoxy substituted thioxanthenes

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Summary

The Photoinitiating activities of a range of mainly novel *n*-propoxy and methyl, *n*-propoxy thioxanthone derivatives in *n*-butyl methacrylate monomer and a commercial triacrylate resin are compared with their spectroscopic and photochemical properties in 2-propanol solution. Photopolymerisation activity is highly dependant on the position of the propoxy group in the thioxanthone molecule with the highest activity being displayed by substitution in the 3-position. In this position the $n\pi^*$ character of the lowest excited triplet state is retained whereas substitution in the 2 and 4-positions introduces a degree of charge transfer character into the molecule. Substitution of methyl groups in the 3 and 4-positions activates the molecule while substitution in the 1-position reduces activity. The spectroscopic and steady-state photolysis experiments indicate that whilst there may be some correlation between the extinction coefficients and photopolymerisation activity of the thioxanthone initiators, the activity of the lowest excited triplet state is also important.

Photopolymerisation studies in the presence of various amines indicates that the ionisation potential of the latter is important implicating the involvement of a triplet exciplex with the thioxanthone initiator which undergoes an initial process of electron transfer. Fourier transform infra-red analysis of chloroform extracted cured resin films confirms that the alkylamino radical produced by a hydrogen atom abstraction mechanism is the species responsible for addition to the acrylate resin and subsequent initiation of the polymerisation and crosslinking reactions.

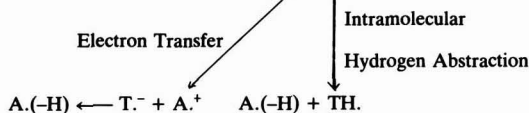
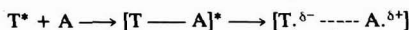
Introduction

Many efforts have been directed toward gaining an understanding of the mechanistic action of photoinitiators under various conditions in order either to develop better quality and more efficient initiator types or to improve formulations¹⁻³. One particular class of photoinitiator is the thioxanthenes which display high photoinitiation activity when irradiated in the near ultraviolet with wavelengths up to 400nm³. This feature makes them particularly valuable for the photocuring of white pigmented coatings⁴.

The efforts in this field have involved a deeper understanding of the mode of initiation of thioxanthone initiators as well as developing novel derivatives in order not only to provide further information on the mechanism of initiation but also as a means of improving photoinitiating activity⁵⁻¹⁰. The results to date indicate two primary mechanisms in initiation of the photopolymerisation of acrylate monomers both of which involve an intermediate exciplex. Both are summarised in Scheme 1, the first involving intramolecular hydrogen atom abstraction from the amine co-synergist to produce a ketyl type radical and

Scheme 1

T=Thioxanthone; TH.=ketyl radical; T.⁻=radical anion; A=Amine; A.⁻=-amino radical; M=monomer



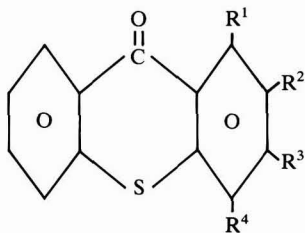
an alkylamino radical while the second involves electron abstraction from the amine to give an amine radical cation. The latter then loses a hydrogen atom to give an alkylamino radical.

It has been established through both spectroscopic and flash photolysis studies that whilst oil soluble thioxanthenes operate primarily through a triplex excited exciplex^{5,7-9}, the water soluble types appear to operate through both a singlet and triplet excited complex^{6,10}. The role of the amine in Scheme 1 is clearly an important factor in the initiation step and much of the research undertaken indicate that the electron transfer step is important. In this paper a photopolymerisation study has been carried out on a range of mainly novel propoxy and methyl propoxy substituted thioxanthenes (Structures I(a-g)) in the presence of various amines to establish the relationship between structure and photopolymerisation activity as well as the importance of the electron transfer mechanism in a commercial triacrylate resin (Structure II) and a vinyl monomer, *n*-butyl, methacrylate. Through a quantitative steady-state photolysis study in the absence and presence of an amine and earlier spectroscopic data information is obtained on the nature of the excited state involved. Evidence is also provided, through the use of Fourier Transform infra-red spectroscopy, for addition of the α -alkylamino radical to the acrylate monomer and not the thioxanthone ketyl radical.

Experimental

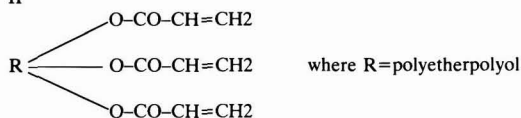
Materials

Samples of chromatographically pure thioxanthenes



- I (a) $R^2=n$ -propoxy, $R^1=R^3=R^4=H$
 (b) $R^3=n$ -propoxy, $R^1=R^2=R^4=H$
 (c) $R^4=n$ -Propoxy, $R^1=R^2=R^3=H$
 (d) $R^1=CH_3$, $R^4=n$ -propoxy, $R^2=R^3=H$
 (e) $R^1=R^4=CH_3$, $R^2=n$ -propoxy, $R^3=H$
 (f) $R^3=R^4=CH_3$, $R^2=n$ -propoxy, $R^1=H$
 (g) $R^1=R^3=R^4=CH_3$, $R^2=n$ -propoxy

II



(Structures I(a-g)) were supplied by Ward-Blenkinsop & Co Ltd, Widnes, Lancashire, UK. Melting points and microanalytical data were reported on earlier⁸. The triacrylate resin (Structure II) was supplied by Lankro Chemicals Ltd, Eccles, Manchester and the n-butyl methacrylate, piperidine, dicyclohexylamine, diethylamine, N-methyldiethylamine, triethylamine and tri-n-butylamine were obtained from the Aldrich Chemical Co Ltd. The solvents chloroform, n-butanone and 2-propanol were all of "Analar" quality and were obtained from Fison's Ltd, UK.

Spectroscopic Measurements

Normal and second-order derivative absorption spectra were obtained using a Perkin-Elmer Model 554 spectrophotometer. Fluorescence and phosphorescence excitation and emission spectra were obtained using a Perkin-Elmer LS-5 luminescence spectrometer. Fluorescence quantum yields were obtained at 300 K using the relative method with quinine sulphate as the standard assuming a quantum yield of 0.55 in 0.1M sulphuric acid¹¹. Phosphorescence quantum yields were obtained at 77 K using the same method but with benzophenone as a standard assuming a quantum yield of 0.74 in ethanol glass at 77°K. All spectra were corrected using a Perkin-Elmer 3600 data station with an appropriate obey file for this purpose. Infra-red spectra were obtained using a Mattson Fourier-Transform spectrometer (Model Alpha-Centauri).

Photopolymerisation Experiments

Rates of photopolymerisation were measured dilatometrically at 30°C utilising a 100W tungsten/halogen lamp at 10 cm distance. n-Butyl methacrylate (50/50 v/v with 2-butanone) was used as the monomer. The initiators and amines were each used at 0.1% w/v concentration.

Photocuring rates, using the triacrylate resin (Structure

II), were obtained on 12µm thick coatings on aluminised polyester film irradiated using a 100W high pressure mercury lamp described earlier³ and measuring the consumption of the acrylate absorption band at 812 cm⁻¹ with respect to the ester band at 1740 cm⁻¹ using reflectance infra-red analysis. The latter absorption band operates as an internal standard compensating for shrinkage effects during the curing process. A Perkin-Elmer model 1400 infra-red spectrometer was used for this purpose. Thioxanthone concentrations used were 0.5 and 1% w/w whereas the amine concentrations were variable and are quoted in the results.

Steady-State Photolysis

Solutions (5x10⁻⁵M) of the thioxanthenes in the absence and presence of N-diethylmethylamine (5x10⁻⁵M) in argon saturated (<1ppm O₂) 2-propanol were irradiated using 365nm monochromatic light isolated from a 200W high pressure mercury lamp using a Bausch & Lomb monochromator. The light intensity was calibrated using potassium ferrioxalate as the actinometer¹².

Results and Discussion

The rates of photopolymerisation of n-butylmethacrylate and the commercial triacrylate resin (Structure II) in the presence of the various thioxanthone initiators (Structures I(a-g)) are compared in Tables 1 and 2 respectively. Here

Table 1

Percentage Conversion of n-Butyl Methacrylate After 10 minutes Irradiation in a Dilatometer in the Presence of Various Propoxy Substituted Thioxanthenes and N-diethylmethylamine (0.5% w/v each)

Thioxanthone (0.5% w/v)	% Conversion (10 m)
2-Propoxy	0.11
3-Propoxy	0.18
4-Propoxy	0.17
1-Methyl-4-Propoxy	0.16
1,4-Dimethyl-2-Propoxy	0.06
3,4-Dimethyl-2-Propoxy	0.20
1,3,4-Trimethyl-2-Propoxy	0.15

Table 2

Percentage Conversion of a Triacrylate Resin After 3 minutes Irradiation in the Presence of Various Propoxy Substituted Thioxanthenes and N-diethylmethylamine (0.5% w/v each)

Thioxanthone (0.5% w/v)	% Conversion (3 m) (812/1740 cm ⁻¹)
2-Propoxy	0.095
3-Propoxy	0.150
4-Propoxy	0.110
1-Methyl-4-Propoxy	0.105
1,4-Dimethyl-2-Propoxy	0.085
3,4-Dimethyl-2-Propoxy	0.230
1,3,4-Trimethyl-2-Propoxy	0.060

Table 3

Spectroscopic Properties of Propoxy Thioxanthenes in 2-Propanol

Thioxanthone	Absorbance		Fluorescence		Phosphorescence	
	λ_{max} (nm)	log E	E_{mlmax}	ϕ_f	E_{mlmax}	ϕ_p
2-Propoxy	385	3.84	463	0.78	490	0.19
3-Propoxy	361	3.75	415	0.13	439	0.34
4-Propoxy	384	3.87	450	0.10	466	0.74
1-Methyl-4-Propoxy	386	3.86	465	0.04	498	0.03
1,4-Dimethyl-2-Propoxy	400	3.81	483	0.22	500	0.03
3,4-Dimethyl-2-Propoxy	400	4.03	460	0.48	491	0.15
1,3,4-Trimethyl-2-Propoxy	385	3.84	455	0.07	480	0.04

the tertiary amine N-diethylmethylamine was used as the co-synergist and whilst the conversion of the n-butylmethacrylate monomer was measured dilatometrically the triacrylate resin was monitored by measuring the decrease in the acrylate absorption band at 812 cm^{-1} . Close similarities in both sets of data are seen. Thus, for n-butylmethacrylate the efficiency of initiation follows the order 3,4-dimethyl-2-propoxy > 3-propoxy > 4-propoxy > 1-methyl-4-propoxy > 1,3,4-trimethyl-2-propoxy > 2-propoxy > 1,4-dimethyl-2-propoxy derivative and for the triacrylate resin the order is 3,4-dimethyl-2-propoxy > 3-propoxy > 4-propoxy > 1-methyl-4-propoxy > 2-propoxy > 1,4-dimethyl-2-propoxy > 1,3,4-trimethyl-2-propoxy derivative. From this data it is evident that substitution of an n-propoxy group in the thioxanthone molecule induces the highest activity when in the 3-position. Substitution of methyl groups induces further activity when in the 3 and 4 positions whilst in the 1-position there is some, although not marked, deactivation. These results may be partly interpreted through the spectroscopic properties of the compounds shown in Table 3. Introduction of methyl groups in the 3 and 4 positions of the thioxanthone molecule red shifts the longest wavelength absorption maximum due to electron donation into the ring system. This induces a higher degree of charge-transfer character into the molecule and, in fact, there is some correlation between the extinction coefficients of the initiators and their photopolymerisation activities. Substitution of a methyl group in the 1-position deactivates the carbonyl group probably due to some degree of weak intramolecular hydrogen bonding. This is reflected by the lower phosphorescence quantum yields shown in Table 3. The 3-n-propoxythioxanthone has the lowest extinction coefficient and shortest wavelength absorption and yet exhibits high photoinitiation activity. Substitution in this position however, induces a much lower degree of charge-transfer character into the molecule thus retaining the activity of the lowest excited triplet nn^* state of the carbonyl group.

Thioxanthone molecules are inefficient photoinitiators when used alone². Their efficiency is very much dependent on the type of amine co-synergist. The results in Tables 4 and 5 demonstrate the influence of amines of varying ionisation potential on the photopolymerisation of n-butylmethacrylate monomer and the triacrylate resin respectively in the presence of 4-propoxythioxanthone. In both cases it is seen that with the exception of piperidine the percentage photoconversion increases with decreasing ionisation potential of the amine. These results confirm our earlier proposal in support of the initial step involving electron transfer via an exciplex shown in Scheme 1. This is

Table 4

Influence of Amines on the Percentage Conversion of n-Butyl Methacrylate After 60 minutes Irradiation in a Dilatometer Using 4-n-Propoxythioxanthone as the photoinitiator (0.1% w/w)

Amine (0.1% w/w)	Ionisation Potential	% Conversion (60 m)
Piperidine	9.76	0.192
Dicyclohexylamine	9.20	0.004
Diethylamine	8.40	0.175
N-Diethylmethylamine	8.10	0.304
Triethylamine	7.85	0.583
Tri-n-butylamine	7.40	0.658

Table 5

Influence of Amines on the Percentage Conversion of a Triacrylate Resin After 3 minutes Irradiation Using 4-n-Propoxythioxanthone as the photoinitiator (0.5% w/w)

Amine (0.5% w/w)	Ionisation Potential	% Conversion (3 m)
Piperidine	9.76	0.06
Dicyclohexylamine	9.20	0.02
Diethylamine	8.40	0.05
N-Diethylmethylamine	8.10	0.11
Triethylamine	7.85	0.20
Tri-n-butylamine	7.40	0.23

further supported by the results in Tables 6 and 7 which show that the photopolymerisation conversions of n-butylmethacrylate and the triacrylate resin increase with increasing concentration of amine (N-diethylmethylamine) in the presence of 4-n-propoxythioxanthone. Thus, amines with a low ionisation potential effect a higher rate of photopolymerisation. The anomalous behaviour of piperidine may well be due to the inactivity of the ring system for abstractable hydrogen atoms although how this would account for an apparent increase in photopolymerisation activity is uncertain. The activity of the N-H however, may contribute to this effect.

Further confirmation of the importance of the amine in initiating photopolymerisation is demonstrated by the results shown in Figure 1. In this experiment thin photo-cured films of the triacrylate resin (Structure II) were refluxed in chloroform for three hours to remove any un-

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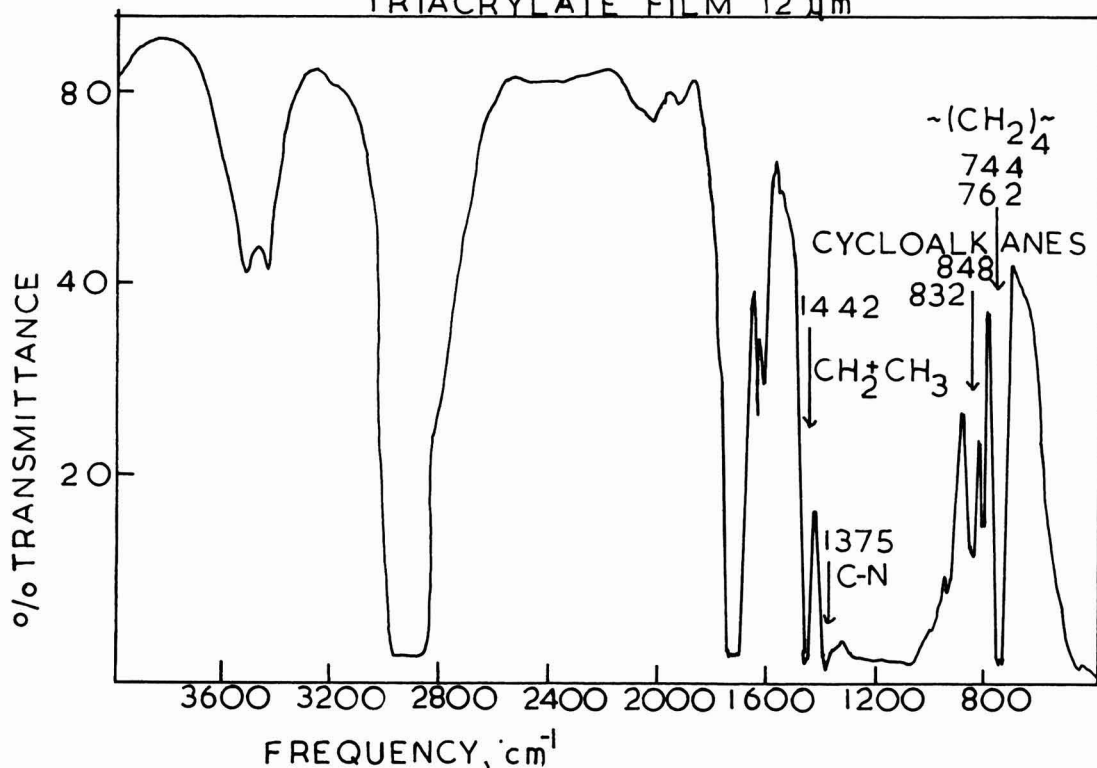


Figure 1. Fourier transform infra-red spectrum of a chloroform extracted photocured triacrylate film (12 μ thick) with 1% w/w each 4-n-propoxythioxanthone and triethylamine.

Table 6

Influence of *N*-Diethylmethylamine Concentration on the Percentage Conversion of *n*-Butylmethacrylate After 30 minutes Irradiation Using 4-*n*-Propoxythioxanthone as the Photoinitiator (0.1% w/w)

Amine (% w/w)	% Conversion (30 m)
0.1	0.09
0.2	1.75
0.3	2.12
0.4	2.40

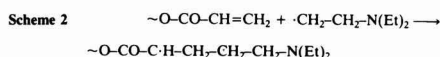
Table 7

Influence of *N*-Diethylmethylamine Concentration on the Percentage Conversion of a Triacrylate Resin After 60 seconds Irradiation Using 4-*n*-Propoxythioxanthone as the Photoinitiator (1% w/w)

Amine (% w/w)	% Conversion (812/1740 cm^{-1}) (60s)
0	0.07
1	0.22
2	0.30
3	0.35
4	0.45

bound residual initiators and their spectra recorded using a Fourier Transform infra-red spectrometer. Initiator and amine concentrations used were 1% w/w. Control spectra of the uncured resin, thioxanthone and amine (triethylamine) were also recorded. The Fourier transform infra-red spectrum of an extracted-cured film (12 μm thick) is shown in Figure 1. After comparison with the control spectra new bands were identified at 1375 cm^{-1} due to the C-N stretch, 1442 cm^{-1} due to vibrational stretching of a combined methylene and methyl group, 848 and 832 cm^{-1} doublet due to a cyclobutane ring and strong doublet band at 762 and 744 cm^{-1} associated specifically with four bonded methylene groups¹³. These bands were not observed in the control spectra apart from the C-N stretch for the amine. The presence of the latter clearly confirms that the alkylamino radical is coupling to the resin whilst the bands at 1442, 762

and 744 cm^{-1} confirm that the active radical is on the β carbon atom of the amine and that this adds directly to the acrylate group thus:



Although hydrogen atom abstraction is believed to occur primarily from the α -carbon atom in the amine this is unstable and is believed to revert to the more stable β -position¹⁻². Our results here would appear to support this earlier hypothesis. The bands at 848 and 832 cm^{-1} indicates

Table 8

Quantum Yields of Photoreduction of Thioxanthenes at 365 nm Irradiation in Argon Saturated 2-Propional in the Absence and Presence of N-Diethylmethylamine ($5 \times 10^{-5} M$)

Thioxanthone ($5 \times 10^{-5} M$)	ϕ (Photolysis) 365nm Alone	ϕ (Photolysis) 365nm + Amine	Acceleration Factor
2-Propoxy	0.0017	0.0740	43.5
3-Propoxy	0.3380	0.5910	1.7
4-Propoxy	0.0100	0.5430	54.3
1-Methyl-4-Propoxy	0.0005	0.0239	47.8
1,4-Dimethyl-2-Propoxy	0.0002	0.0016	8.0
3,4-Dimethyl-2-Propoxy	0.0017	0.0300	17.6
1,3,4-Trimethyl-2-Propoxy	0.0024	0.0065	2.7

crosslinking across the acrylate groups to give a four membered cyclobutane ring system.

This accelerating effect of the amine on the photopolymerisation activity of thioxanthone initiators is clearly an important factor. The results in Table 8 compare the quantum yields of photoreduction of the thioxanthenes in de-oxygenated 2-propional in the absence and presence of an amine namely, N-diethylmethylamine. Such an experiment carried out under monochromatic irradiation allows us to quantify more accurately the acceleration factors involved. The quantum yields of photoreduction bear a close similarity to the rates of photopolymerisation in Tables 1 and 2 with the 3-propoxythioxanthone displaying an abnormally high quantum yield. Indeed this latter result confirms the presence of a lowest excited triplet n^* state being involved in the photoreduction. All the other thioxanthenes exhibit much lower quantum yields due to the presence of a lower lying charge-transfer state. In the presence of the amine however, much higher quantum yields are observed and acceleration factors of up to 54, in the case of 4-propoxythioxanthone, were measured. In fact, the quantum yields of photolysis in the presence of the amine correlate closely with the phosphorescence quantum yields shown in Table 3 supporting the involvement of a triplet exciplex in the photoreduction mechanism.

Conclusions

These results provide evidence in support of a mechanism involving a triplet exciplex in the photopolymerisation of acrylate monomers and resins by thioxanthone initiators with an amine co-synergist. Electron abstraction is the primary mechanism of photoreduction followed by hydrogen abstraction from the amine to give an alkylamino radical. The latter then adds on to the acrylate group initiating polymerisation.

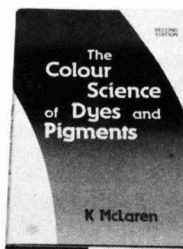
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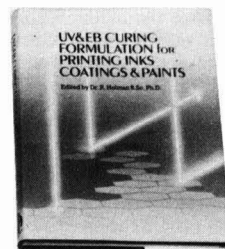
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New Approach to the Effect of Binder Composition on Antifouling Efficiency Using Scanning Electron Microscopy

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Summary

The work in the present article is restricted to vinyl copper paints containing a high percentage of cuprous oxide as the main toxin. Two vinyl copolymers were used in paint formulations, they were externally plasticized by two different plasticizers. Rosin was included at two levels, one of which is considered to be a relatively high content. Painted films were immersed in a salt solution and film surface changes were studied using a scanning electron microscope. Film properties are interrelated with the leaching behaviour, and raft tests of the prepared compositions will be presented in another article.

Introduction

An antifouling paint must be accurately formulated so that a gradual removal of some ingredients takes place at a controlled rate to prevent adherence of fouling organisms on submerged surfaces in the sea. The secret in formulating a good antifouling paint lies in the selection of toxins of suitable lethality and to incorporate them in a medium of a suitable permeability to allow the formation of a laminar layer rich in toxic materials to spread over the paint film.

Contact copper paints represent an important group of antifouling compositions in which cuprous oxide is introduced in the formulation at relatively high levels. Copper leaching from the paint film would occur through a diffusion-dissolution mechanism^{1,2}. Sea Water diffuses through the active part of the antifouling layer, where cuprous oxide particles dissolve, then the dissolved copper ions diffuse to the boundary layer at the surface of the paint film. The rate of dissolution of copper depends not only upon the water characteristics in contact with the paint film but also on some factors relating to the paint ingredients. Hydrological factors affecting copper release such as salinity, pH temperature and agitation have frequently been studied by many investigators^{3,4}. Studies on the effect of paint ingredients on copper leaching were limited to a few parameters such as cuprous oxide content^{3,5}, and the effect of non-toxic pigment fillers and extenders⁶⁻⁸. With regard to the binder ingredients rosin has been found to be of interest to some investigators^{3,9,10,11}. The importance of incorporating rosin in most antifouling compositions lies in the fact that its acidic properties will accelerate the leaching of toxins into the slightly alkaline sea water. Studies by Ghanem and Abd El-Malek¹² showed that rosin should be added carefully in the formulation of a contact copper paint to achieve the highest antifouling efficiency. They also found that the type of plasticizer in vinyl copper paints has a great role in the antifouling properties of the formulation¹³.

In order to extend the life of vinyl copper paints, cuprous oxide was incorporated in a set of formulations at the maximum level usual in conventional copper paints, and the cuprous oxide content was kept constant in all the formulations. Changes were made in the binder ingredients

such as the type of vinyl copolymer, the type of external plasticizer and the rosin content. Laboratory and raft results showed that the binder composition greatly affects the paint film properties¹⁴.

The aim of the present work is to investigate the role of binder ingredients on the behaviour of high copper content vinyl paints. It was decided to study the changes in paint film surfaces after storage in a salt solution. Thus, painted films of two groups of formulations differing in their binder composition were immersed in a laboratory storage tank. Film surfaces were investigated periodically using a scanning electron microscopy technique essentially similar to that applied by Bishop and Silva¹⁵.

Experimental

Paint compositions

Four antifouling compositions divided into two sets were prepared. The first set comprised two formulations based on Vinyl Resin I, a vinyl chloride-vinyl acetate copolymer with tricresyl phosphate (TCP) as external plasticizer. The second set also comprised two formulations based on Vinyl Resin II, a vinyl chloride-vinyl isobutyl ether copolymer, with a polvinyl methyl ether as external plasticizer Rosin WW and a micronized grade of cuprous oxide were also used in the paint formulations.

Laboratory samples were prepared by dispersing paint ingredients, using a highly efficient centrifugal ball mill. The fineness obtained was below 10 microns and was measured using a Hegmann grindometer. Paint viscosity was adjusted for application and the paints filtered before use. Dry paint film compositions are shown in Tables 1 and 2.

Panel preparation

Sheets of impact resistant PVC were cut to panels of 80x50x3 mm³ dimensions and were roughened with sand paper. Test panels were painted with two coats using a film applicator forming uniform dry films of approximately 80 microns.

Test panels were immersed in a synthetic salt solution of 3.8% NaCl and the pH was adjusted at 8 to 8.2. The solution was renewed from time to time and stirred with a steady stream of air bubbles.

Scanning electron microscopy technique

The test panels were removed biweekly from the leaching bath and the specimens gold coated using a modified E 5000 Polaron Cool Sputter Coater. Every coating was earthed using a conductive silver paint. The specimens were usually about one square centimetre in area. The thickness

Table 1

Dry Film Composition of Set I Formulations Based on Vinyl Copolymer and Hydrolyzable Plasticizer

Paint No.	AF ₁		AF ₂	
	% by Wt.	% by Vol.	% by Wt.	% by Vol.
Ingredient				
Vinyl Copolymer I	11.10	28.80	3.10	7.60
Tricresyl Phosphate	2.80	9.36	2.80	8.83
Rosin WW	4.20	14.01	12.20	38.43
Cuprous Oxide	81.90	47.83	81.90	45.14
Pigment/Binder	4.52	0.92	4.52	0.82
Rosin/Binder	0.22	0.26	0.63	0.70
Total Solubles	88.99	71.20	96.90	92.40

Table 2

Dry Film Composition of Set II Formulations Based on a Swellable Vinyl Copolymer and Swellable Plasticizer

Paint No.	AF ₃		AF ₄	
	% by Wt.	% by Vol.	% by Wt.	% by Vol.
Ingredient				
Vinyl Copolymer II	11.40	30.88	4.10	11.00
Polyvinyl methyl ether*	3.50	9.81	1.80	4.99
Rosin WW	4.20	13.44	12.20	38.63
Cuprous Oxide	81.90	45.87	81.90	45.38
Pigment/Binder	4.52	0.85	4.52	0.83
Rosin/Binder	0.22	0.25	0.64	0.71
Total Solubles	88.60	69.12	95.90	89.00

*Plasticizer

of the film was calculated to be about 300 Å. The specimens were then examined using a scanning microscope, model JSM3 produced by Jeol Ltd., Japan. Magnification power was in the range of 800-880 X.

Results and Discussion

Scanning Micrographs

Investigation of a large number of micrographs of the antifouling paint films taken periodically showed that appreciable changes occurred on the film surfaces. Surface changes were observed during the first two weeks of immersion. Figures 1 to 4 are the scanning micrographs of the four tested formulations after 30 days' immersion. All micrographs revealed some degree of surface roughness and film porosity, which varied from one formulation to the other. The micrographs also showed that there is a good contact among cuprous oxide particles which are encased within a thin layer of the binder. No unpigmented areas were observed, indicating the sufficiency of pigment content in relation to the binder portion. The micrographs were also characterized by the presence of appreciable numbers of pores and voids. Evolution of film pores and voids confirms the findings of Bishop and Silva¹⁵ in their study on the effect of pigment volume concentration (PVC) on the surface texture of vinyl-Cu₂O paint films. They concluded that rough and porous films were obtained at 60% PVC which was much lower than an earlier value calculated as 74%.³ That value (74%) was postulated to achieve hexagonal packing of the cuprous oxide particles in the formulation, assuming that they are spherical in shape and homogeneous in size. The 60% value obtained on applying simple formulations consisting of cuprous oxide

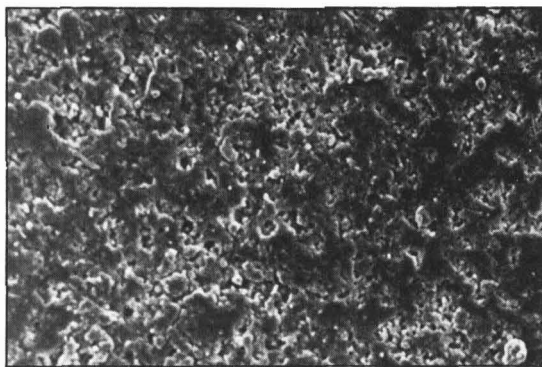


Figure 1. Vinyl Copolymer-TCP-Low Rosin, AF₁, after 30 days' immersion. Magn. x 800.

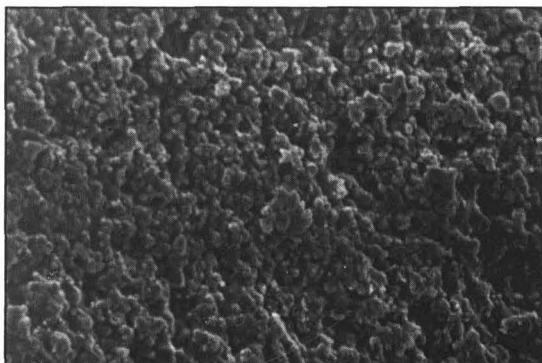


Figure 2. Vinyl Copolymer-TCP-High Rosin, AF₂, after 30 days' immersion. Magn. x 880.

and unplasticized vinyl copolymer¹⁵. In the present work, pigment content of the tested formulations is not more than 48%, which is considered to be a relatively low value in comparison with previous ones. Of course, pigment content, particle size and shape have direct effects on surface roughness and film porosity. On the other hand, the chemical characteristics of both pigment and binder constituents will greatly affect paint film texture as will be shown from the following discussions.

Set I Micrographs (AF₁ & AF₂)

From the first sight of these micrographs, two main results can be extracted. The first is the high degree of compactness among cuprous oxide particles and the second is the increase in number and size of pores in AF₁ over AF₂ (see Figures 1 and 2). As the pigment content is the same in both formulations, these differences in surface texture are attributed to variations in the binder composition. As shown in Table 1 the only difference between AF₁ and AF₂ lies in their rosin contents, respectively 14% and 38% in AF₁ and AF₂. Both formulations contain liquid plasticizer (TCP) in the same amount 10%. Good compaction between cuprous oxide particles in this set of formulations is attributed to the good wetting properties of both rosin and TCP, with low molecular weights and weak cohesive forces between their molecules¹⁷. In particular, rosin as an acidic material readily wets basic pigments like cuprous oxide. In addition, the reaction product between rosin and cuprous oxide during paint milling or storage forms copper rosinate, which is a liquid, and this greatly facilitates the

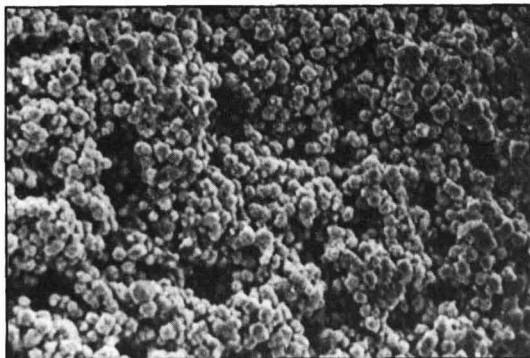


Figure 3. Swellable Vinyl Copolymer-Swellable Plasticizer-Low Rosin, AF₃, after 30 days' immersion. Magn. x 800.

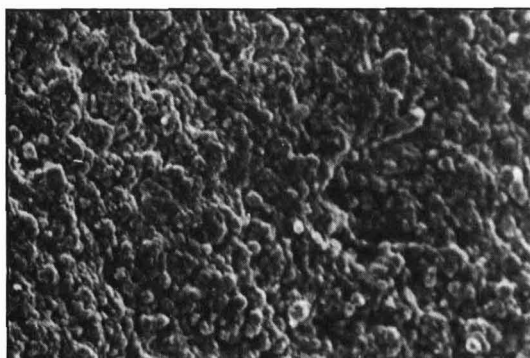


Figure 4. Swellable Vinyl Copolymer-Swellable Plasticizer-High Rosin, AF₄, after 30 days' immersion. Magn. x 880.

wetting process and fills the voids between pigment particles. Consequently, it can be said that the number of pores and voids in the paint surface of AF₁ are greater than AF₂ mainly due to the rosin content.

Set 2 Micrographs (AF₃ & AF₄)

The common feature characterising these micrographs is the high degree of surface roughness in comparison with Set 1 micrographs as shown in Figures 3 and 4. A rough surface has a larger area than a smooth one of the same nominal dimensions. Hence the active area for toxin release will be increased, resulting in an increase in the antifouling potential of the formulation.

Again, there is a distinct difference in number and size of pores between AF₃ and AF₄ which is mainly attributed to their rosin content as discussed before under Set 1.

In comparing the two sets of micrographs, it can be seen that the degree of surface roughness as well as the number and size of pores in Set 2 are higher than those of Set 1 micrographs. Differences in surface texture between the two sets are attributed to the type of the vinyl copolymer and its external plasticizer used in the formulations. In Set 1 formulations, the vinyl copolymer used was a vinyl chloride-vinyl acetate which exhibits little degree of hydrolysis and its role in copper release can be ignored. The external plasticizer was tricresyl phosphate which is a liquid, hydrolyzable ester and could migrate easily through highly porous paint films. Rapid release of soluble

materials in the paint film such as cuprous oxide, rosin and other hydrolyzable ingredients is accelerated in the presence of a hydrolyzable plasticizer especially during initial periods of immersion. This finding is confirmed by study of the scanning micrograph of AF₂. As shown in Figure 2 there are dark patches spread on the surface of the micrograph indicating the formation of green precipitates of compounds as a result of the high initial copper leaching rates. Copper leaching values either in accelerated or normal leaching tests confirm clearly this finding. Leaching results of the tested formulations which are discussed in detail in another article¹⁴ are relevant to this point. As shown in Table 3 copper leached out in glycine extraction increases with the rosin content and is affected to some extent by the type of plasticizer.

Table 3
Glycine Test Results

Composition No.	Rosin Content % by Vol.	Type of plasticizer	mg Cu/cm ² /3 days*
AF ₁	14.01	Hydrolyzable	3.59
AF ₂	38.43	Hydrolyzable	4.59
AF ₃	13.44	Swellable	2.33
AF ₄	38.36	Swellable	4.23

*Optimum level is 2.3 mg Cu/cm²/3 days

High copper values were recorded in the glycine test with 4.59 and 4.23 mg/3 days for AF₂ and AF₄ whose rosin contents were 38.43 and 38.36%, whilst AF₁ and AF₃ had lower amounts of leached out copper 3.59 and 2.33 mg with a rosin content of 14.01 and 13.44% comparison between amounts of extracted copper from AF₁ and AF₃ indicates that the hydrolyzable plasticizer in AF₁ increases the copper leaching process to some extent.

The results of the normal laboratory leaching rate test over a period of one year are presented in Figures 5 and 6. It is shown that all formulations gave steadily adequate leaching rates above the optimum value of 10 µg Cu/cm²/day. In comparing the initial areas of the leaching curves, it can be seen that high values of leaching rates were recorded for AF₂ and AF₄, in agreement with the accelerated leaching results obtained by the glycine test.

It is known that contact copper paints leach out excessive quantities of copper during early periods of immersion in sea water^{3,16}. High copper concentration in the boundary layer diminishes the rate of dissolution of cuprous oxide particles embedded in the attacked layer (or the active part) in the paint film. (Figure 7 is a diagram of a cross section in an antifouling layer showing its different parts.) In addition, high copper concentration in the boundary layer lead to precipitation of basic copper salts (basic copper carbonate and copper oxychloride) which clog the film pores resulting in suppression of the copper ion flow from the paint film interior to its outside.

It can be said that incorporation of a high rosin content coupled with the liquid hydrolyzable plasticizer in one formulation greatly accelerates copper release, especially during the initial periods of immersion. The rapid and excessive copper release will greatly reduce the leaching rates during the steady-state leaching periods.

On the other hand, incorporation of the swellable ingredients, the vinyl copolymer and its external plasticizer,

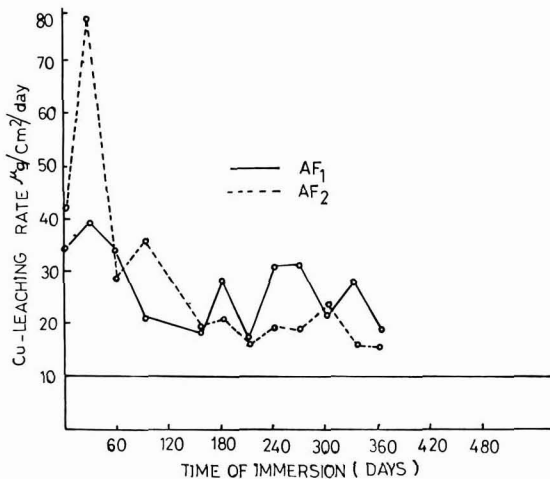


Figure 5. Cu leaching rate of AF₁ and AF₂ versus immersion time.

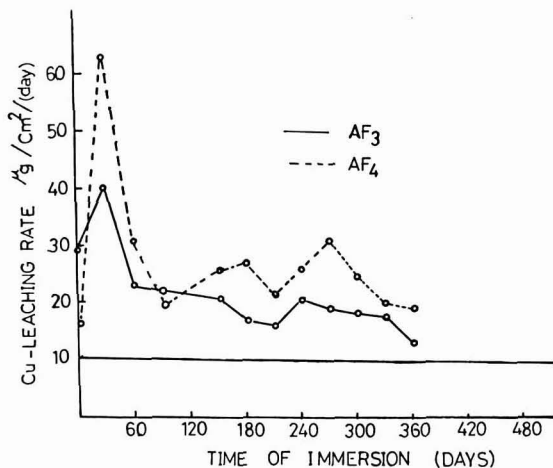


Figure 6. Cu leaching rate of AF₃ and AF₄ versus immersion time.

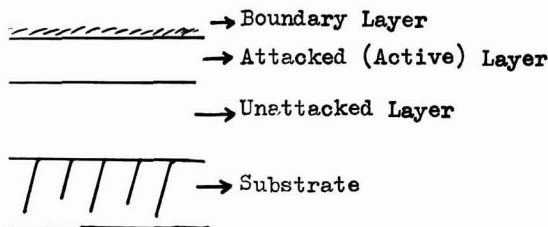


Figure 7. Diagram of a cross section in an antifouling paint film.

used in Set 2 formulations is considered as a good modification in contact copper paints. The swellable binder permits a small amount of water to be retained permanently in the film interior, especially throughout the attacked (active) part of the antifouling layer. Retained water provides a good chance of long contact between water molecules and bare or encased cuprous oxide particles. Dissolution either direct from bare cuprous oxide particles

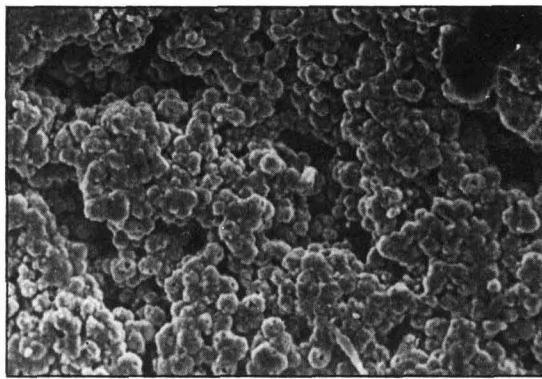


Figure 8. Swellable Vinyl Copolymer-Swellable Plasticizer, Low Rosin, AF₄, after 45 days' immersion. Magn. x 880.

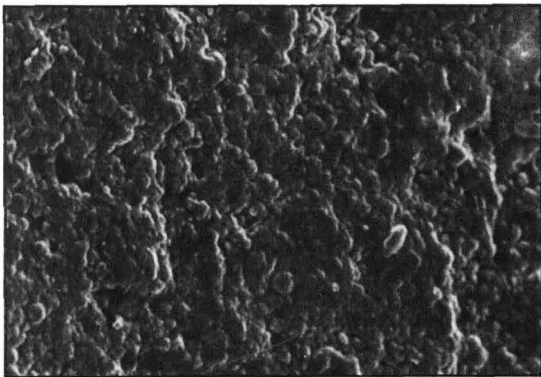


Figure 9. Swellable Vinyl Copolymer-Swellable Plasticizer-High Rosin, AF₄, after 45 days' immersion. Magn. x 880.

or from coated particles after rupturing the binder shell will maintain the copper concentration throughout the attacked part of the film which will be higher than its concentration in the boundary layer. Thereby the flow of the dissolved copper complexes from the paint film interior to the surface is continued at an adequate rate for longer periods than formulations based on unswellable binders.

It can be also said that the attacked part in the swollen film might increase gradually with time during its storage in salt solution through a slow migration of the retained water molecules into the unattacked part of the film. This result can be seen from the scanning micrographs of AF₃ and AF₄ after 45 days' storage. As shown in Figures 8 and 9, the scanning micrographs illustrate that there is an appreciable increase in the size of cuprous oxide particles due to increase in the swellability of the binder shells encasing them. So, it seems that a swollen film will act as a sponge-like material which controls copper release at an adequate rate above the optimum value of 10 µg Cu/cm²/day. This conclusion can be confirmed from raft results in the eastern harbour of Alexandria. Figure 10 shows that AF₃ and AF₄ exhibited antifouling potential up to 436 days much better than AF₁ and AF₂.

Conclusions

Scanning electron microscopy is a valuable technique for studying surface changes of antifouling paint films of different binder compositions. The presence of a liquid

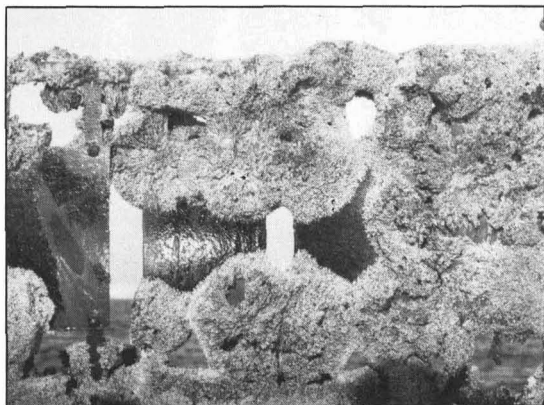


Figure 10. Raft Testing of AF₂, AF₃ and AF₄ after 436 days' immersion in Alexandria Eastern Harbour.

hydrolyzable plasticizer coupled with a high rosin content in the binder composition makes the cuprous oxide particles tighter and in closer contact with each other, resulting in the reduction of film pores and voids. High soluble contents in such formulations lead to rapid and excessive copper leaching, particularly during the initial periods of immersion. Heavy surface deposits will be formed which suppress the flow of dissolved copper complexes from the film interior to its outside, especially during the steady-state leaching period. Hence, such formulations have limited antifouling efficiency in warm fouling-rich waters.

Swellable ingredients in the binder composition increase the size of the active (attacked) layer of the antifouling film, due to prolonged contact between water molecules and cuprous oxide particles. A swellable paint film acts as a sponge-like material throughout with the concentration of dissolved copper complexes being higher than its concentration in the boundary layer. Thus the copper ion flow continues for longer periods than with unswellable paint films.

Acknowledgement

This work was sponsored and supervised by the late Prof. N. A. Ghanem. To his memory we present this work.

The authors wish to express their deepest gratitude to the staff at the International Technical Centre for Rubber and Plastics (RAPRA), Shawbury, England, for their continuous help and facilities offered for this work, especially the use of their Scanning Electron Microscope.

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Following the presentation of each paper at the OCCA Conference a period of time was allotted for discussion. Those who put the questions were asked to fill in discussion slips with the details of their question. Edited versions of the discussion (recently received) that followed one of the papers (authors in bold) published in the July issue appear below: questions in ordinary roman type, answers in italic. Only those questions for which discussion slips were received are published.

Durability of anti-carbonation coatings by H Robinson, presented by S A Hurley of Taywood Engineering.

H MESNER: Has there been any experience in Europe of Rebar Coatings reducing damage?

S A HURLEY: For repair to carbonated concrete, there should be no need to use coatings on the rebar, as the cementitious repair mortar will restore the alkaline environment around the cleaned, rust-free bar. However, evidence from Germany suggests that use of certain types of rebar coating, particularly those containing cement clinker, increase the likelihood of a durable repair being made, as such coatings tend to compensate for improper bar preparation. Within the UK, opinions differ, with manufacturers recommending a variety of bar treatments varying from a cement slurry to a zinc-rich anti-corrosion primer. Where chlorides (eg CaCl_2) are present either alone or in combination with carbonation, the position is less clear. It has been shown that a preferential electrolytic corrosion process is stimulated in areas adjacent to the patch repair. Work needs to be undertaken to evaluate the phenomenon.

Until such time, the only method whereby such electrolytic corrosion has been prevented is by use of an impressed current cathodic protection system.

L J BOWMAN: Could the speaker comment on the apparent contradictory requirements of preventing ingress of CO_2 into the concrete, whilst providing water vapour permeability from the concrete into the atmosphere? Should the coating be totally impermeable, or should it be "breathable"? How does one achieve the balance between these requirements?

S A HURLEY: A successful anti-carbonation coating works by reducing to insignificant levels the rate of penetration of atmospheric CO_2 into the concrete. This is achieved by forming a closed film which is relatively impermeable to the diffusion of CO_2 at the recommended thickness. The continued satisfactory performance of the coating depends on maintaining its coherency, which may be affected by weathering of the film (eg chalking or hydrolysis) or, in the short term, a break-down in its adhesion to the concrete leading to blistering. The exact causes of blistering on concrete are not clearly understood, but the prime suspect is the presence of moisture at the coating/concrete interface. Such moisture can be present as a result of applying coatings to wet concrete or be caused by the temperature gradient from the inside to the outside surfaces of the building. Under solar action, the collected water vaporizes and can generate pressures which are sufficient to cause blistering. To prevent this build-up of water, the coating should allow the passage of water vapour, allowing the building fabric to dry in periods of low ambient relative humidity.

Certain coatings will allow the passage of vapour, but not CO_2 because two completely different fundamental transport mechanisms are operating. CO_2 is transported by a purely gaseous diffusion mechanism, whilst water is transported by a solution diffusion mechanism incorporating absorption/desorption processes. Thus, a coating can provide both the essential protective requirements (ie prevent the passage of CO_2) and allow potentially damaging water vapour to

escape. However, as the exact nature of the blistering mechanism is not fully understood, the critical limit for the vapour diffusivity of a coating is somewhat nebulous.

R J WOODBRIDGE: Further to the last discussion, experience has shown that certain quality emulsion based products can give very good CO_2 resistance whilst having a high level of water vapour permeability. This has been confirmed both by testing in Germany and by Taywood Engineering.

S A HURLEY: Our results to date show that certain types of emulsions have a CO_2 resistance similar to the more widely accepted barrier coatings (ie Urethanes, Solvented, Acrylics etc). When considering the use of an emulsion-based coating the over-riding consideration must be its long-term durability, measured in terms of its fundamental weathering characteristics, which has traditionally been considered worse than for barrier coatings.

To date, only a few emulsions have been found to provide the necessary durability characteristics. With increasing environmental awareness, this is clearly a key development area which is already well advanced in Germany. With advancing paint technology, formulators may soon be able to produce emulsions which can equal the durability of solvented coatings.

J BERNIE: What are the differences in characteristics for coatings applied to new and shallowly carbonated concrete?

S A HURLEY: In terms of their CO_2 barrier resistance properties, coatings applied to shallowly carbonated concrete will have to perform better than those applied to new construction; this assumes the same grade of concrete and cover to steel are used and equal life expectancies are required. This is because there is less concrete to be carbonated in the older structure before the rebar becomes active. It is possible to calculate theoretically the required performance for an anti-carbonation coating, based on the concrete parameters given above. For example, a new structure may only need a coating with an R-value of 5m, whereas for a badly carbonated concrete, a figure in excess of $R=50\text{m}$ after weathering may be an essential requirement.

Coatings applied to new concrete probably require a higher water vapour transmission rate (ie of the order 50-100 $\text{g/m}^2/24\text{h}$). This is because the 'green' concrete has a very high loss of water during its formative early months. When coatings are applied onto a mature concrete (ie >2 years old) the W.V.T.R. is perhaps not as critical and coatings with values as low as 10 $\text{g/m}^2/24\text{h}$ may prove acceptable.

R J WOODBRIDGE: Can Eric French comment on the relevance of Agreement certificates to the building industry, giving confirmation of 10 year durability of exterior coatings. An increasing number of exterior products have now been awarded certificates which should support the industry's claims of acceptable durability over 10 years and more?

S A HURLEY: We find it difficult to conceive how a new

conference discussions

coating or other product can be guaranteed without evidence of its long-term performance after say 10 years under natural exposure conditions. Guarantees without a documented track record, even if individual components of the product have performed adequately, must be considered of dubious value. Accelerated weathering trials can provide guidelines as to performance of a product, but at the present time there

does not exist any tangible correlation between natural and accelerated weathering. In these circumstances, data from accelerated weathering tests should not be relied upon for guarantee purposes. These comments should not detract from the value of Agreement Certificates in terms of the quality assurance the independent verification gives the specifier and end user.

occa meetings

London Section

20 years on

The first meeting of the London OCCA section entitled "20 years on" took place on Thursday, 17 September 1987 at "The Naval Club", 38 Hill Street, off Berkeley Square W1. This was a departure from the venue of recent years, however, from the comments of approval made by the members it suggests that the choice of this prestigious venue was the right one.

The choice of speaker to launch this new season of lectures, proved a great success in Mr Michael Brent, chairman of Trimite Ltd, who reviewed the changes in fortune of the top 24 UK paint companies of 1966-67 up to the current year.

Tables comparing the performance of the top 18 public and 6 private UK companies of '66-'67 were displayed. Of these 24 companies, only the bottom 2 were then in a loss making situation. This compared with the 24 top UK companies of '87, where the bottom six now find themselves in a loss making position, a drop in performance by a factor of 3!

Mr Brent went on to compare the survival rates between the private and public sector. From the original 6 family

companies found in the 1967 list of top 24 UK companies, 3 have survived, a survival rate of 33.3%. However, from the 18 public companies included in the '66-'67 top 24, only 3 have survived, a survival rate of 16.67%, half that of the private sector.

He continued by quoting from current research which points to family companies out-performing their private counterparts in every area.

Finally, he argued that family businesses invoke a degree of commitment and loyalty from their staff which is difficult to produce in public companies.

In conclusion, he stated that Trimite Ltd, is now the largest privately owned UK paint company and was looking with confidence to the challenge of the next 20 years. And for those wishing to know what the future holds for the current top 24 UK companies, he offered the following advice: "If you want to know the future, look at the past".

This stimulating and often humorous talk, was well received by an audience whose lively participation had been encouraged during the talks "quiz sessions." During these sessions, the audience were invited to demonstrate their knowledge of the UK paint companies history.

A vote of thanks to Mr Brent for this interesting and well presented talk and also for the hospitality extended by Trimite was proposed by Dr Hamburg.

P C Neal

occa news

Chester Conference Column



"Profitable Research & Development" has been chosen as the main theme for the Chester 89 International OCCA Conference. For the first time, the conference has been broadened to encompass the important commercial aspects of product research and development. Papers will be presented on the commercial development of new products, instruments and machinery for the Surface Coatings Sector.

Authors will show how their products go through several stages in their formation i.e. from conception within the laboratory to their development in the company followed by the market research and marketing of their product to the consumer.

John Taylor will report in more detail in a subsequent issue but in the meantime,

we look forward to hearing from members and non-members who wish to participate.

professional grade

At the meeting of the Professional Grade Committee held on 15 July 1987 the following admissions were made:

Admitted to Associateship

Holmes, Peter Neville (*Irish*)

Russell, George Rowland Michael (*Transvaal*)

Admitted to Licentiatehip

Gill, Trevor George (*London*)

Mulji, Ajai (*London*)

Transvaal Visitor



David Lindsay (Vice Chairman, Transvaal Section) on the right being welcomed by Chris Pacey-Day (Gen. Sec. OCCA) to Priory House.

OCCA Goes On-Line



FROM THE GENERAL SECRETARY

As the first stage of the modernisation of the Priory House offices, the Association has recently taken delivery of a micro-computer. The computer system has very largely been funded by a generous donation from the Manchester Section and will initially be used to maintain the register of members, run the Association's accounts and provide word processing facilities for the offices. The equipment is based upon an AST micro-computer, one of the best of the IBM look-alike computers on the market and includes a tape back-up system for copying of data. In consequence of the move to a computer based register of members, the Association has registered under the Data Protection Act and will therefore provide an annual facility for members to update their personal profiles. In addition to the computer the Association has also purchased a high speed printer which will be used to produce labels for the



Mr Pacey-Day initiating the OCCA staff computer training programme at Priory House

monthly mailings of JOCCA. A programme of staff training has already been initiated and it is hoped that by the end of the year all current membership information will be loaded on to the computer so that by early 1988 members will be receiving their Journals mailed under labels produced by the new system. An early advantage of the system to members will be that it will enable alterations in personal details and in particular address changes to be simply added to the data-

base, ensuring that the Journals are sent to the correct addresses and the labels should look more attractive than at present! The second phase of the computer project will see the installation of another micro-computer and letter quality printer which will be used for word processing and for some desk top publishing. The installation of the computer will help to provide a more professional image of the Association and a better service to members and is a welcomed and necessary provision.

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SITA Selection

- Liquid Inks 'In Plant' Technologist** for major company with strong growth in the liquid inks market, 27-35, with five years experience. NORTH **£14,000 p.a. + car + commission**
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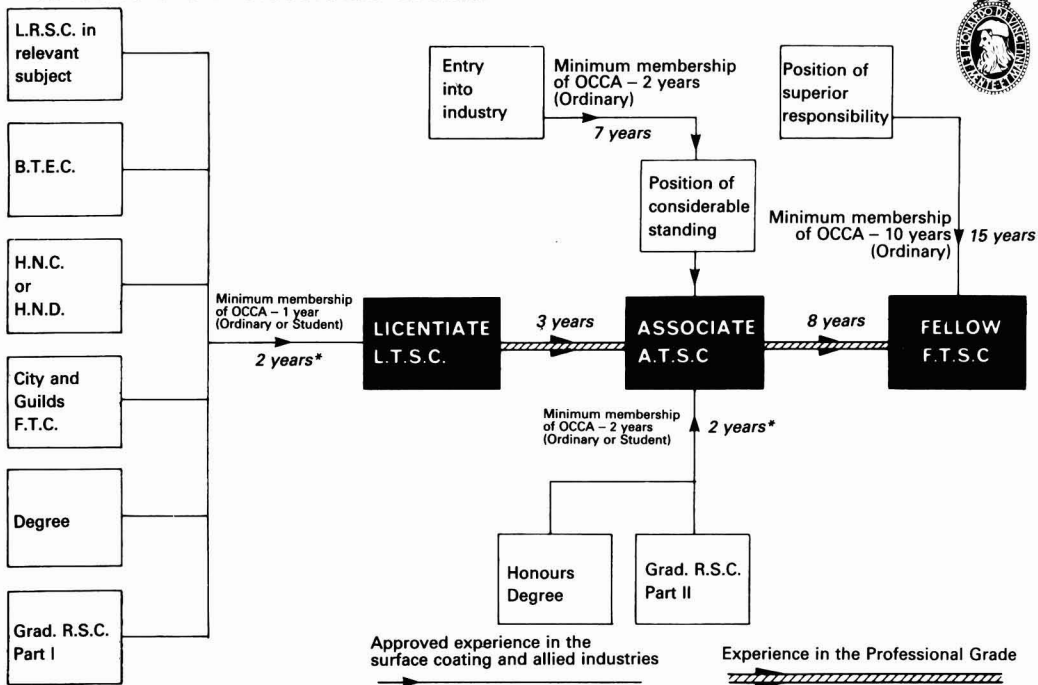
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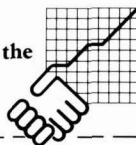
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