



J  
O  
C  
C  
A

OCCA-31

**EXHIBITION**

3-6 April 1979  
Alexandra Palace, London



CLOSING DATE FOR  
APPLICATIONS FOR SPACE  
**31 OCTOBER 1978**



# JOURNAL OF THE IL & COLOUR CHEMISTS' ASSOCIATION

Electroinduced polymer coatings

*J. D. Scantlebury, V. Ashworth and B. Yap*

Molecular weight fractionation experiments with alkyds *J. D. Frazee*

Mechanisms of efflorescence resistance in paint films *J. Boxall*

The photocatalytic oxidation of liquid phase propan-2-ol by pure rutile and titanium dioxide pigments

*R. B. Cundall, B. Hulme, R. Rudham and M. S. Salim*

The role of the Diels-Alder reaction in the curing of drying-oil alkyd-melamine systems

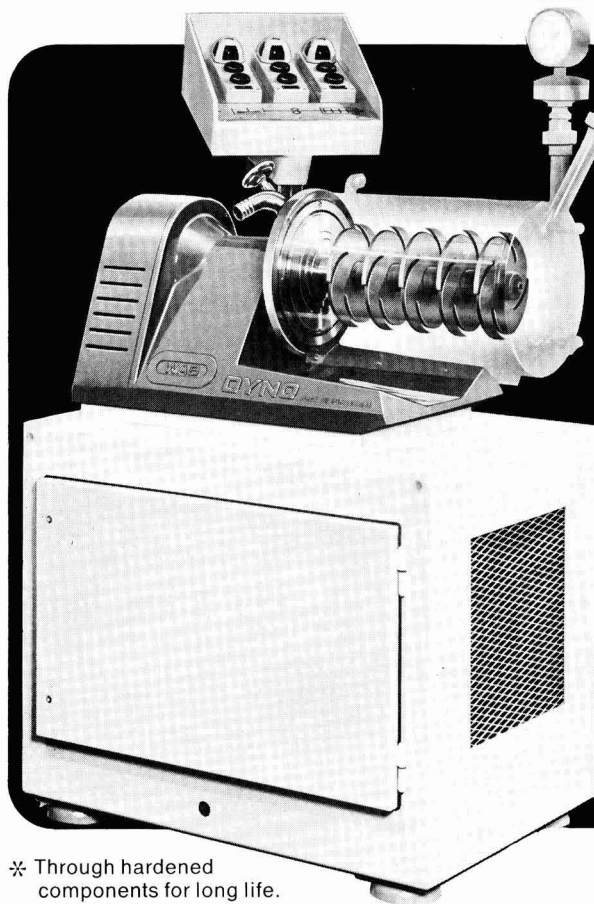
*K. Holmberg*

The mechanism of the acid catalysed curing of alkyd-melamine systems

*K. Holmberg*

# DYNO-MILL<sup>®</sup> FROM GLEN CRESTON

for superior paints  
and inks at lower cost



There is much more to a DYNO-MILL<sup>®</sup> than a horizontal cylinder!

- ✧ *Dyno-Mills have no screens to get clogged or to be replaced at a crippling cost year after year. Instead, a simple, self-cleaning and patented dynamic separator is used. Made of tungsten carbide, it lasts for many years and is easily adjusted to suit beads of any size.*
- ✧ *In what other bead mill could you replace a shaft seal for £3?*
- ✧ *With each Dyno-Mill, Glen Creston provide expert advice, meticulous commissioning of new plant, free training of your personnel and fast after-sales service.*

- ✧ *Through hardened components for long life.*
- ✧ *Simplicity of design for minimal maintenance.*
- ✧ *Superb Swiss engineering for lasting reliability.*
- ✧ *Beads of glass, ceramic, steel, etc., can be used.*

**With hundreds of machines in service throughout the world, many five years in continuous operation, can you afford to settle for less than the Dyno-Mill, the mill that revolutionized paint technology?**

Please write to us or telephone for full details, prices and demonstrations either in our applications laboratory (just 10 minutes drive from the M1 motorway) or on your own premises.

 **Glen Creston**  
Machinery Limited

16 Carlisle Road, London NW9 0HL, England.  
Telephone: 01-200 1666. Telex 925791.  
Telegrams: Glencrest London NW9.

*Enquiries outside the UK and Eire please address direct to the manufacturers.*

 **WILLY A. BACHOFEN**

Mfg. Engineers, Dept. of Application Technology, CH 4000  
Hasle 5, Switzerland. Tel: 061-33 55 55. Telex 62564

# SYNTHETIC ESTERS



## TECHNICAL FATTY OILS SPERM, FISH, NEATSFOOT AND LARD OILS

### HIGHGATE AND JOB LIMITED

35 REGENT ROAD, LIVERPOOL L5 9TB  
Phone: 051-207 0447  
MURRAY STREET, PAISLEY Phone: 041-889 3207

**AT YOUR SERVICE to develop finer, more durable products**

The fast, economical weather tests of

### SUB-TROPICAL TESTING SERVICE, INC.

established 1929

Sub-Tropical Testing Service is known and utilised world wide

Our 50th year



Send for free  
Sub-Tropical colour  
brochure

Sub-Tropical Testing gives fastest Natural Weather tests available for ★ paints  
★ chemical coatings ★ plastics ★ textiles ★ fabrics ★ related products ★

*(List of representative clients given upon request)*

Wir waren die ersten, welche einen Prüfdienst dieser Art für Lacke, Kunststoffe, chemische Beschichtungen, Stoffe und Gewebe aller Art, Farbstoffe und verwandte Erzeugnisse in den U.S. möglich machten.

Mr. C. Hubbard Davis, Founder, Sub-Tropical Testing Service, Inc. (1904-1977)  
P.O. Box 560876, 8290 S.W. 120th Street, Miami, Florida, U.S.A. 33156

Phones: (305) 233-5341  
Cable: SUBTROP, Miami



# TOP SECRET VARNISHES

Hardmans oleo-resinous varnishes are the secret ingredients used by leading paint manufacturers.

Our modern plant and high technology ensure close compliance with the most stringent specification. We have no connections with any paint manufacturer.

Contact us for an oleo-resinous varnish quotation to your own specification (treated in confidence), or from our own range.

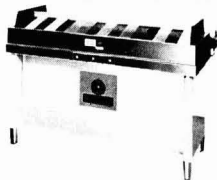
Hardmans know all the secrets.

## HARDMANS

Varnish makers to the paint industry

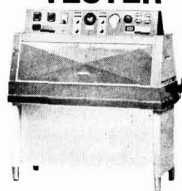
E. Hardman, Son & Co. Ltd.  
Bedford Street, Hull, North Humberside  
HU8 8AX  
Tel: (0482) 23901

### CONDENSATION TESTER



The QCT Condensation Tester tests finishes for resistance to moisture in the form of rain and dew. The QCT's unique condensation system gives faster, more realistic tests than conventional humidity, while maintaining foolproof control of water purity, oxygen saturation, and test temperature. Initial cost is quite low, and maintenance is almost nil. Ordinary tap water may be used, because the QCT distills the water in the process of transporting it to the test surface. Test severity can be varied widely by regulating the temperature.

### ACCELERATED WEATHERING TESTER



The QUV Accelerated Weathering Tester has replaced conventional methods of durability testing in hundreds of labs throughout the world. The QUV simulates rain and dew by the same mechanism as our QCT Condensation Tester. The effects of sunlight are simulated by an array of 8 special fluorescent lamps. Light emission is concentrated in the critical UV wavelengths, providing closer control and faster testing. Users report excellent correlation with outdoors.

Initial cost is a fraction of competing testers, and annual operating costs are thousands of pounds less than carbon arc or xenon arc machines. Electrical consumption is just 700 watts. Operation is completely automatic, with a wide variety of temperatures and cycles easily programmed. Scheduled maintenance is just 15 minutes once a month.

### TEST PANELS

The Q-Panel Co. is the world's largest manufacturer of steel and aluminium panels for paint testing. Millions of Q-Panels are used every year because of their consistently high surface quality and remarkably low price. Q-Panels are available in a variety of sizes and finishes.

### THE Q-PANEL CO.

15610 Industrial Pkwy. • Cleveland, Ohio 44135 U.S.A.  
Phone (216) 267-9200

# färg och lack

## färg och lack

The only Scandinavian Magazine  
inside the Paints and Varnish industry.

**Journal for members of Skandinaviska Lackteknikers Förbund  
(Federation of Scandinavian Paint and Varnish Technologists)**

Färg och Lack is received by all engineers and technicians employed in the Scandinavian Paint and Varnish Industry. This means that there is 100 % coverage of the potential market.

The objective of the journal is to inform about research results and other topics which are of interest to the paint and varnish industry, its technicians and suppliers in the Scandinavian countries.

**The geographical distribution of readers is app.:**

**Denmark 26 %, Finland 10 %, Sweden 39 %, Norway 25 %**

Advertisement department:

**20, HOLBERGSGADE  
DK-1057 COPENHAGEN K, DENMARK**

**Phone (01) 14 06 11**

Advertising manager Leif Nesgaard

## J. O. C. C. A.

*is our advertisement*

Similar Publications, Weekly, Monthly or Quarterly are our speciality. Reports and accounts, internal stationery and advertising literature in colour are all produced speedily and efficiently at our North London plant which has over one hundred experienced staff working in two shifts at your service.

**Richard Madley Ltd**

**P.O. Box 151, Elthorne Road, London N19 4AH**

Tel 01-263 0256

ZINC OXIDE — “Zincoli” Brand

ZINC DUST — “Zincoli” Brand

IRON OXIDE — “Deanox” Brand  
Reds, Yellows and Marigold

RED LEAD — “Deanox” Brand

DISPERSIONS — “Ashby” Pigment  
Dispersions

ASPHALTUM — “Gilsonite”  
(Regd. Trade Mark)

Can be supplied in  
all grades suitable for  
the requirements of the  
Paint and Varnish Industry

by

**MORRIS ASHBY LIMITED**

10 PHILPOT LANE, LONDON, EC3M 8AB

Phone:

01-626 8071 (6 lines)

Telegrams:

ASHBY, LONDON

Telex: 886170

*And at Liverpool, Glasgow, Birmingham and Leeds*

*Agents throughout the world*



**English China Clays Extender Pigments can improve **OPACITY** by developing the hiding and pigmenting powers of prime pigment and cut your costs!**

The ever increasing costs of titanium dioxide make it vitally important for manufacturers to utilize so expensive a material to maximum effect.

The use of an ECC Extender Pigment can achieve optimum spacing between prime pigment particles. Properly used, it can also improve working qualities and create economies in prime pigment utilization.

Take ECC "Speswhite", for

instance – a very fine china clay of exceptional brightness, ideal for the current trend towards semi-gloss or satin finishes. At a fraction of the

cost per tonne of titanium dioxide, this functional pigment can utilize and extend the properties of the prime pigment effectively, more efficiently.

It is just one example of how an ECC Extender Pigment can become a cost-effective ingredient of your formulation – whatever type of emulsion you are producing.

To find out more, and to obtain authoritative technical literature, contact our Marketing Manager, Roland Simpson.



**ECC International**  
**PAINT & POLYMER DIVISION**

**Paint works better with ECC Extenders.**

ECC International Ltd., John Keay House, St. Austell, Cornwall, England.  
 Telephone: St. Austell 4482. Telex: 45526 ECCSAU G.



**Croda**

I am interested in the following resins  
Please send me literature  samples   
Name \_\_\_\_\_  
Company \_\_\_\_\_  
Address \_\_\_\_\_

Send off the coupon for full details of our products.

Croda Resins Ltd  
Crabtree Manorway Belvedere Kent DA17 6BA  
Tel Enith 31631 Telex 896384  
Choosing the right resin to formulate your particular coating can be difficult. So take your cue from us—choose Croda

# Choosing a resin? Play safe with Croda

**Plastokyd** oil free polyesters

**Kelrez** printing ink resins

**Laquanol** water thinnable resins

**Hythane** polyurethane resins

**Plastokyd** silicone co-polymers

**Hylex** printing ink media

**Plastamid** polyamide resins

**Plastokyd** alkyd resins

**Plastoprene** cyclised rubber resins

**Plastokyd** alkyd resins

**Plastrol** acrylic resins

**Plastrol** monomer modified alkyd resins



# JOURNAL of the OIL AND COLOUR CHEMISTS' ASSOCIATION

Hon. Editor: S. R. Finn, BSc, FRIC, FTSC

Contents

Vol. 61 No. 9

September 1978

*Publications Committee:*

R. McD. Barrett, BSc, MSc  
 G. D. E. Carroll  
 R. A. C. Chappell, MRIC  
 R. K. Chater, BSc  
 T. Entwistle  
 A. W. Fell, BSc, AMCT, ATSC  
 C. N. Finlay, ATSC  
 P. A. J. Gate, BSc, ARIC, FTSC  
 H. R. Hamburg, PhD, FTSC  
 T. Harbottle  
 A. MacDonald, ATSC  
 W. McDonald  
 A. McLean, BSc, ARCST, FRIC, FTSC  
 D. J. Morris  
 A. J. Newbould, BSc  
 D. Pountain  
 F. D. Robinson, BSc, ATSC  
 T. W. Slinn, BSc, FTSC  
 D. M. Smith  
 F. M. Smith, BSc, PhD, MRIC, FTSC  
 A. R. H. Tawn, FRIC, FinstPet, FTSC  
 J. R. Taylor, BSc, FRIC, FTSC  
 A. J. Walbridge, MA, BSc  
 T. W. Wilkinson, AMCT, FTSC  
 D. S. Wilson  
 F. B. Windsor, ATSC

Editorial correspondence should be addressed to the Hon. Editor, *JOCCA*, 49 Elms Drive, Kirk Ella, Hull HU10 7QH

General correspondence should be addressed to:  
 R. H. Hamblin, MA, FCIS,  
 Director & Secretary,  
 Oil & Colour Chemists' Association  
 at the address below.

Tel: 01-908 1086  
 Telex 922670 (OCCA Wembley)  
 Telegrams: OCCA Wembley Telex

Assistant Editor: D. M. Sanders

Annual subscription to non-members: £30.00 (\$60), post free by surface mail, payable in advance.

Single copies £3.00 (\$6), post free by surface mail, payable in advance.

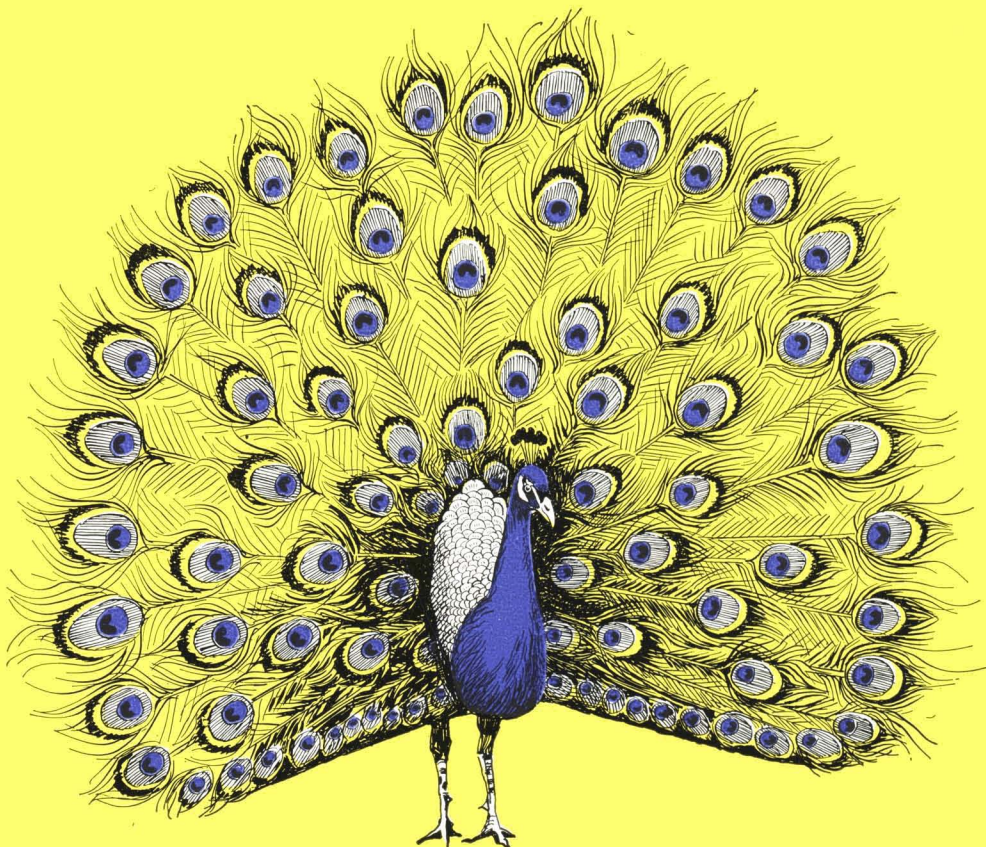
*Transactions and Communications*

<b>Electroinduced polymer coatings</b> . . . . .	335
<i>J. D. Scantlebury, V. Ashworth and B. Yap</i>	
<b>Molecular weight fractionation experiments with alkyds</b>	341
<i>J. D. Frazee</i>	
<b>Mechanisms of efflorescence resistance in paint films</b>	345
<i>J. Boxall</i>	
<b>The photocatalytic oxidation of liquid phase propan-2-ol by pure rutile and titanium dioxide pigments</b> . . . . .	351
<i>R. B. Cundall, B. Hulme, R. Rudham and M. S. Salim</i>	
<b>The role of the Diels-Alder reaction in the curing of drying-oil alkyd-melamine systems</b> . . . . .	356
<i>K. Holmberg</i>	
<b>The mechanism of the acid catalysed curing of alkyd-melamine systems</b> . . . . .	359
<i>K. Holmberg</i>	
<i>Correspondence</i> . . . . .	362
<i>Section Proceedings</i> . . . . .	362
<i>Review</i> . . . . .	363
<i>Information Received</i> . . . . .	363
<i>Notes and News</i> . . . . .	365
<i>Register of Members</i> . . . . .	367
<i>Forthcoming Events</i> . . . . .	368

Published by

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

*The Honorary Editor, the Council and the Oil and Colour Chemists' Association do not accept responsibility for opinions expressed by correspondents or contributors to this Journal. The contents of the Journal are copyright and permission to reproduce Transactions and Communications, in full or in part, must first be obtained from the Honorary Editor*



## COLOURS

for the Paint, Printing Ink, Plastics, Rubber,  
Flooring and Linoleum Industries

**Kenkrom**

Lead and Zinc Chrome Colours

**Organics**

Permanent Yellows G and 10G  
Benzidine Yellows and Orange

### E. P. BRAY & COMPANY LIMITED

Coombes Lane Works,  
Charlesworth,  
Hyde, Cheshire.  
Telephone: Glossop 3277  
Telex: 667523

*Southern Sales & Accounts,*  
206 Mitcham Road,  
London, S.W.17.  
Telephone: 01-672 6514

# Electroinduced polymer coatings\*

By J. D. Scantlebury, V. Ashworth and B. Yap

Corrosion Protection Centre, UMIST, P.O. Box 88, Manchester M60 1QD

## Summary

A novel method of coating mild steel by an electrochemical method using an alkaline solution of phenol is described. It is shown that by controlling the composition of the electrolyte solution and the electrode potential of the specimen a thin, continuous and electrically insulating coating may be applied. It is suggested that this

may form the basis of a protective coating technique for ferrous and other materials. Potentiokinetic and potentiostatic techniques supported by scanning electron microscopy have been used to study the film formation.

## Keywords

*Types and classes of coatings and allied products*  
corrosion resistant primer

*Types and classes of structures or surfaces to be coated*  
steel

*Miscellaneous terms*  
electro polymerisation

## Revêtements polymères électro-amorçés

### Résumé

On décrit une nouvelle méthode pour revêtir l'acier doux au moyen d'une méthode électrochimique qui se sert d'une solution alcaline de phénol. On démontre que, par le contrôle de la composition de la solution d'électrolyte et du potentiel d'électrode de l'échantillon, on peut appliquer une couche, mince, continue et isolante électriquement. On suggère que cette méthode pourrait

constituer la base d'une technique pour appliquer les revêtements protecteurs aux matériaux ferreux et autres. Afin d'étudier la mode de formation du film, on a utilisé des techniques photo-kinétiques et potentiostatiques en conjonction avec la microscopie électronique à balayage.

## Elektroinduzierte Polymerbeschichtungen

### Zusammenfassung

Beschreibung einer neuartigen Methode der Beschichtung von Eisenblech durch ein elektrochemisches Verfahren, bei welchem eine alkalische Phenollösung benutzt wird.

Es wird gezeigt, dass durch Kontrolle der Zusammensetzung der Elektrolytlösung, sowie des Elektrodenpotentials der Spezimen

dünne, kontinuierliche und elektrisch isolierende Beschichtungen aufgebracht werden können. Diese Methode könnte die Grundlage für eine Schutzanstrichtechnik für eiserne und andere Materialien bilden. Potentiokinetiche, sowie potentiostatische Techniken wurden unter Mitbenutzung von Abtastelektronenmikroskopie eingesetzt, um die Filmbildung zu studieren.

## Introduction

*Refs. 1-11*

Conventional methods of combating the corrosion of metals frequently involve the use of organic coatings in combination with reactive pigments. The latter have been shown to inhibit corrosion of the underlying metal by a variety of mechanisms<sup>1,2</sup>. In some instances the pigment itself possesses limited solubility (chromate and phosphate pigments) and produces ions that inhibit metallic corrosion, whereas in other cases, the inhibitors are thought to be formed by a chemical reaction between the pigment and the binding medium (lead pigments in combination with drying oils). However, many of the more successful systems, including those containing lead and chromium pigments, are becoming environmentally unacceptable. Furthermore, there is a move away from solvent-based systems to water-based coatings into which it is difficult to incorporate successfully many of the existing pigments. The development of coatings which overcome these objections and difficulties is receiving widespread attention.

For many years chemists have used electrochemical techniques to carry out organic synthesis<sup>3</sup>. An early, and perhaps the most well known, example is the Kolbe synthesis<sup>4</sup> in which metal salts of organic acids yield hydrocarbons on electrolysis. Currently, many similar electrochemical reactions find industrial application<sup>5</sup>.

It has been noted by a number of workers that, under certain specific conditions of electrode potential and electrode and electrolyte solution composition, an electrode becomes coated with an insulating deposit which inhibits further reaction at the electrode and such conditions are to be avoided in electrosynthesis. For example, Pickett *et al*<sup>6</sup> investigated the electrochemical regeneration of phenol from sodium phenoxide solutions using an iron cathode, a lead anode and an intervening cation exchange membrane. The authors reported that a major problem in this work was the fouling of the anodes due to resin formation due to the oxidation of the phenol. The fouling could only be overcome by a change in the composition of the electrolyte solution. Wawzonek<sup>7</sup> studied the electrolytic oxidation of anilines in acetonitrile

\*Revised version of a lecture presented at the Symposium on 'Film formation and behaviour' held by the Manchester Section on 6-7 April 1976.

containing sodium perchlorate and pyridine on platinum with a view to forming azo compounds. He found that within the compositional range used, a decrease in the limiting current for the oxidation was caused by the formation of a coating on the anode. Mieluch<sup>8</sup> investigated the possibilities of using electrochemical techniques to oxidise phenol from industrial effluents and also noted the phenomenon of electrode fouling at certain anodic overpotentials.

In a few instances the film forming characteristics of the reaction during electrosynthesis have been examined. Dijkstra *et al*<sup>9</sup> investigated a variety of phenols in non-aqueous solutions and observed the production of polymer films on the anode. Nine metals, together with silicon and tin oxides, were reported to have been coated successfully. The coatings were said to be decorative, rather hard, but easily damaged. Shimizu *et al*<sup>10</sup> also studied the electrochemical formation of solid polymers on platinum from aqueous acid solutions of phenol and extended their investigation to include the determination of the kinetic rate constants for the reactions.

Prater<sup>11</sup> investigated the anodic oxidation of ring substituted anilines on platinum in tetraethyl ammonium perchlorate. He examined compounds having electron withdrawing and electron donating groups in the *o*- and *m*- positions and found filming reactions when the substituent group was both in the *m*- position and electron donating. These particular substitutions were thought to activate the aniline ring at two positions which were then presumed to be sites for electrophilic attack yielding polymeric material.

The work described in this paper is a preliminary investigation into the feasibility of using film formation by electropolymerisation as a means of coating metals to produce a protective primer. Here the film formation only is examined. Phenol, in aqueous alkali solution, was used as the starting monomer. This compound was chosen because its use eliminated the environmental objections to the conventional primers already outlined, and utilised the body of knowledge built up around organic electrosynthesis. Mild steel, the most common structural material, was used as the electrode to be coated. Standard electrochemical techniques, *viz* the determination of electrochemical polarisation curves and current-time transients at constant electrode potential were used with scanning electron microscopy in the investigation.

Finally, it may be noted that the process described here is not the same as electrodeposition, although certain elements are common to both processes. The major difference is that whereas in electrodeposition most of the polymerisation is carried out either prior to dissolution in the bath or during stoving afterwards, in electropolymerisation, the reaction is thought to take place at, or near the electrode surface during coating.

## Experimental

### Mild steel electrodes

Mild steel panels (15×12×1mm) were cut from sheet material having the following analysis:

Fe	C	S	Si	Mn	Cu
99.02%	0.24%	0.04%	0.05%	0.55%	0.1%

The panels were pickled in 14w/v per cent hydrochloric acid at 30°C until the surface appeared clean, followed by careful rinsing in a series of beakers containing doubly distilled water. Specimens which were used to determine the electrochemical

polarisation curves were given no further surface preparation, but after a final rinse in acetone, were dried and stored in a desiccator. In contrast, specimens that were used in current-time transient experiments and were examined subsequently by scanning electron microscopy, were polished mirror flat (to a 1µm diamond paste finish). After rinsing as above, the specimens were stored in a desiccator.

Some hours before an experiment, and after at least 24 hours' storage, the mild steel panels were connected to a rigid conductor rod and backing plate. The whole assembly was masked using an alkali resistant stopping-off medium (Fortolac, W. Canning and Co. Ltd.) leaving only 1×1cm<sup>2</sup> of the panel surface exposed.

### Test solution

The compositions of the test solutions used are given in Table 1.

Table 1  
Composition of the test solutions

Solution number	Mole ratio phenol/sodium hydroxide	Composition*		pH
		Phenol (g/1000gH <sub>2</sub> O)	NaOH (g/1000gH <sub>2</sub> O)	
1	1:1 equimolar	123.82	52.66	12.4
2	1:2 excess NaOH	95.34	81.12	13.1
3	2:1 excess phenol	145.51	30.96	10.1
4	0:1 NaOH	0	52.67	13.1

\*the phenol/sodium hydroxide solutions contain 15%w/w dissolved solids

### Electrochemical cell and electrical circuit

The electrochemical experiments were made in a conventional electrochemical cell having a capacity of 1000cm<sup>3</sup> and fitted with a multi-necked lid. The counter electrode was a platinum foil (20×10×0.1mm). A saturated calomel electrode was used as the reference electrode, electrolyte contact being achieved by a Luggin capillary probe.

The electrical circuit comprised a potentiostat (Hermes Series 50) to control the electrode potential of the mild steel, a high impedance millivoltmeter (Keithley Instruments 610C) for measuring the working electrode potential and a potentiometric recorder (Servoscribe RE 541 20) to monitor cell current.

### Experimental procedure

Before each electrochemical polarisation experiment the working electrode was immersed in the test solution for approximately 15 minutes to obtain a steady potential. Thereafter the specimen was polarised cathodically to a potential 300mV negative to the rest potential for five minutes to remove the air-formed oxide film.

In determining the electrochemical polarisation curves the potential of the specimen was then raised by 100mV at 5 minute intervals, whilst the current was recorded continuously. The most noble electrode potential reached in the experiment was +2250mV (SHE).

In experiments to determine the current time transient, following the five minute cathodic polarisation, the potential was raised to a pre-selected value in the anodic region by a

single step. The anodic current was recorded continuously at the new potential for up to 100 minutes.

Specimens from the latter experiments were examined by scanning electron microscopy to investigate the morphology of any films formed. The specimens were mounted and coated using standard techniques and examined in the microscope (Stereoscan Mark IIA, Cambridge Instrument Co. Ltd.) at an accelerating voltage of 20kV.

## Results

All electrode potentials reported in this section are referred to the standard hydrogen electrode.

### Electrochemical polarisation

The results of anodic polarisation of the mild steel are shown in Fig. 1. Curve 4 refers to the phenol-free sodium hydroxide solution and shows that initially on increasing the potential from  $-50\text{mV}$  the current is relatively independent of potential (the metal is passive), but thereafter the current rises very rapidly. This latter region is accompanied by visible oxygen evolution on the mild steel, and this reaction undoubtedly accounts for the current rise; there was no evidence of macro-film formation. Curve 2 shows the polarisation behaviour in the presence of phenol and excess sodium hydroxide. The electrochemical results are similar to those obtained in the presence of sodium hydroxide alone, but it was noted that a loose black deposit formed on the steel surface. Again oxygen evolution was observed at the electrode in the higher potential region.

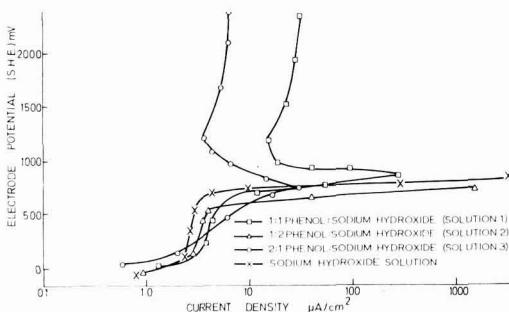


Fig. 1. Electrochemical polarisation curves for mild steel in various phenol/sodium hydroxide solutions

The solutions containing excess phenol (Curve 3) and equimolar concentrations of phenol and sodium hydroxide (Curve 1) show markedly different behaviour from the solutions described above in that visible oxygen evolution was not observed at potentials up to 2250mV. Furthermore, in solution 1 the working electrode changed colour at approximately 1000mV. In contrast, in solution 3 no visible changes occurred. Nevertheless, the abrupt fall in current at approximately 850mV and the absence of oxygen solution is consistent with insulating film formation in each case.

### Current-time transients at constant potential

Using the results of the electrochemical polarisation experiments, two potentials within the region where the oxygen evolution reaction had been suppressed in solutions 1 and 3 were selected for study. The lower potential (850mV) is found in the region where the oxygen reaction is first inhibited, the

higher (1250mV) where any film produced might be expected to be fully formed.

At both 850 and 1250mV, solution 2 produced a visible film on the electrode within a few minutes of raising the potential. This film eventually developed into a thick black deposit but, as the current transients show (Fig. 2) it did not hinder the progress of the electrode reaction significantly. Further, higher currents than those observed in the absence of phenol were recorded and suggest that the film forms by oxidation of the phenol. Whilst solution 1 also gave a black deposit at 850mV, solution 3 gave no obvious film although a colour change to a pale yellow was noted on the electrode surface. For these latter solutions the current transients suggest that some reaction product with insulating properties does form on the surface.

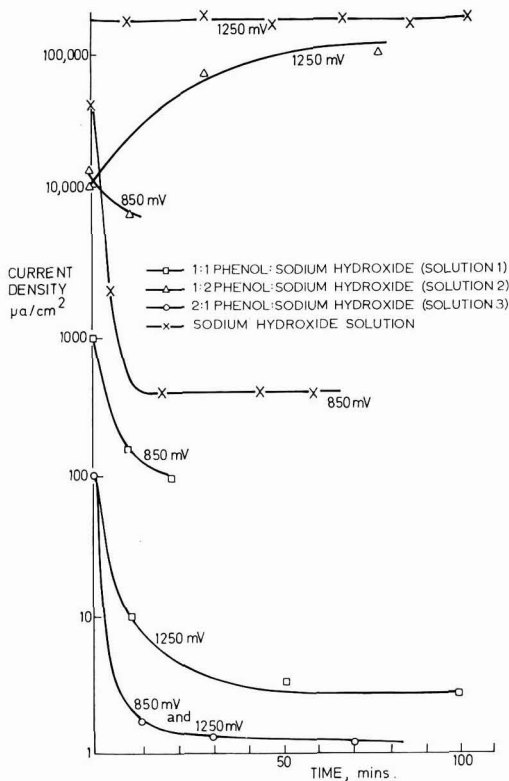


Fig. 2. Potentiostatic current-time transients for mild steel in various phenol/sodium hydroxide solutions

### Scanning electron microscopy

Figs. 3 to 9 are typical scanning electron micrographs of the specimens from the current-time transient experiments. It is clear that a thick film is formed in the presence of excess caustic soda (Figs. 3 and 4). The film shows poor adherence and is highly cracked with some evidence for the cracking following the direction of the scratch marks on the substrate. Such a film would not be expected to be protective and would have limited effectiveness in hindering electrochemical reactions. At the lower potential (+850mV), the equimolar phenol-

sodium hydroxide solution produced a patchy film (Fig. 5) which at higher magnification can be seen to have regular unidirectional cracks (Fig. 6) within the patchy areas. On the other hand, raising the electrode potential in this same solution to 1250mV produced a featureless surface (Fig. 7). However, a visual examination of this specimen indicated a colour change in the surface and, during SEM, there was a pronounced tendency for the specimen to charge-up even at the low voltages used. This indicates the presence of a thin and perhaps continuous film. An entirely similar

surface was produced after short term (<120 minutes) exposure at both potentials in the presence of excess phenol. However, long term exposure (>10 hours) did produce some areas of preferential film growth, appearing as pustules in Fig. 9. No evidence was obtained on the nature of the sites of this preferential growth. Polarisation in the absence of phenol (Fig. 8) even at +2250mV produced no obvious surface film and the specimen retained its bright polished appearance.

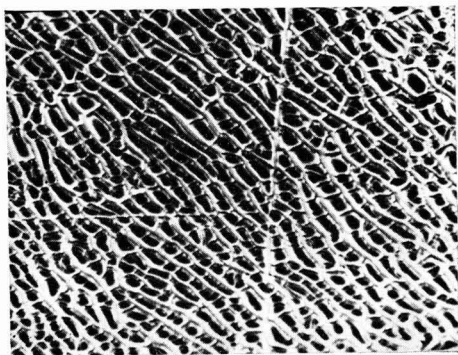


Fig. 3. 1:2 phenol:sodium hydroxide 850mV; 1 min;  $\times 200$



Fig. 4. 1:2 phenol:sodium hydroxide 850mV; 1 min;  $\times 1000$

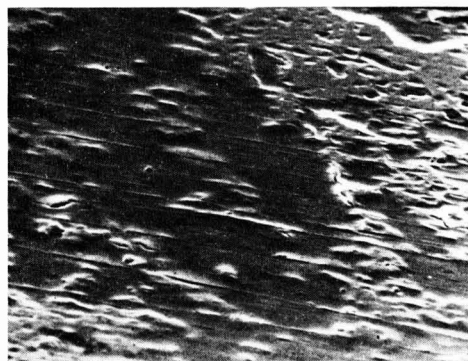


Fig. 5. 1:1 phenol:sodium hydroxide 850mV; 10 min;  $\times 500$



Fig. 6. 1:1 phenol:sodium hydroxide 850mV; 10 min;  $\times 2000$

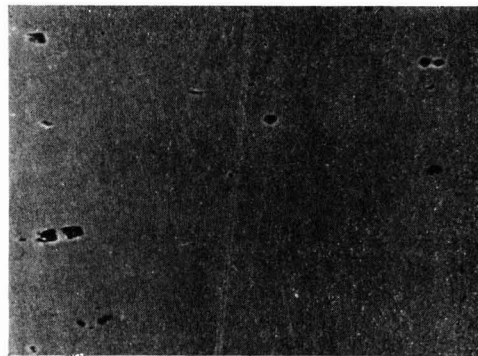


Fig. 7. 1:1 phenol:sodium hydroxide 1250mV; 10 min;  $\times 1000$

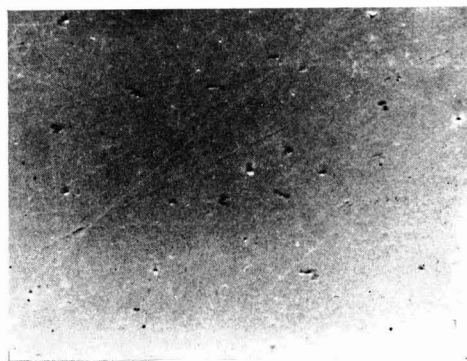


Fig. 8. 0:1 phenol:sodium hydroxide 2250mV; 10 min;  $\times 1000$

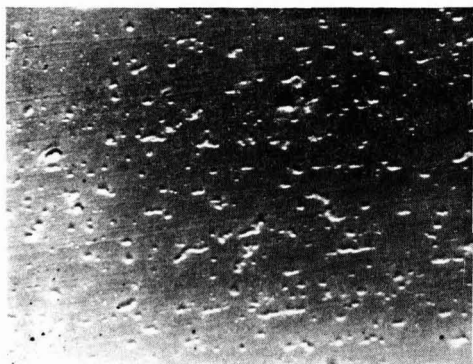


Fig. 9. 2:1 phenol:sodium hydroxide 1250mV; 15 hours;  $\times 1000$

## Discussion

Refs. 12-14

The polarisation curve for mild steel in sodium hydroxide solution, pH 13.1 (Curve 4, Fig. 1) shows typical behaviour with a passive region extending to  $+750\text{mV}$ . Thereafter, a rapid increase in current density with increasing potential occurs due to the onset of the oxygen evolution reaction. Curve 2, determined in the presence of excess sodium hydroxide, has a very similar appearance and again the oxygen evolution reaction takes place at large anodic overpotentials. Sodium phenolate and excess phenol (Curves 1 and 3 respectively) produce markedly different behaviour. In both solutions the electrode exhibits a quasi active-passive transition at ca.  $850\text{mV}$  and at higher potentials the oxygen evolution reaction, and any other anodic reaction extant, are markedly suppressed.

Two reasons may be advanced for the anodic inhibition. Firstly, it is possible that the phenolate ion, or some related species, is chemi- or phys- sorbed on to the surface of the polarised metal at high potentials. Gilcadi<sup>12,13,14</sup> examined the inhibition of the anodic oxidation of bromide and iodide ions on platinum by phenols. In each case the initial stage of the inhibition appeared to be due to the adsorption of the phenolate radical. In the present investigation, however, such adsorption, and therefore the anodic inhibition, would be expected to occur in solution 2 as well as in solutions 1 and 3, since the former contains a significant quantity of phenolate ion and there appears no reason why the formation of the free radical should be hindered. Nevertheless, anodic inhibition is not observed in solution 2 in practice. Furthermore, in postulating inhibition by adsorption, it must be doubted whether such a mechanism would provide an instantaneous reduction in current at a reproducible potential. The second possibility which proves more plausible, is that inhibition is due to film formation. Since the effect is observed only in the presence of phenol, it appears that the film forms from, or its formation is catalysed by, the phenol. However, in only one of the solutions in which inhibition was observed was a visible change in the surface observed.

Several features of the current-time transient results (Fig. 2) reinforce the evidence of the polarisation experiments. Firstly, in the presence of phenol and excess sodium hydroxide, higher currents are sustained than are recorded in the presence of sodium hydroxide alone. It appears that the additional current is consumed in the electrochemical oxidation of phenol. The formation of a visible, loose, black

deposit on the metal shows that the oxidation can form an insoluble product. Attempts to characterise this product by IR spectroscopy suggest that it is a polymeric product. In contrast, both at  $850$  and  $1250\text{mV}$ , solutions 1 and 3 sustain a falling current with time. Indeed in solution 3, although the electrode did not become covered by a visible film, the current falls to approximately  $1\mu\text{A}/\text{cm}^2$ . In the absence of phenol (solution 4), and especially at  $1250\text{mV}$ , the current was many orders of magnitude greater under conditions where once again a visible film was not formed. Since the latter specimen was covered by an oxide film, the difference in the behaviour in the presence of phenol is extremely important. The rapid fall in current with time is more consistent with progressive and continuous, insulating film formation from phenol than with inhibition by adsorption. Very clearly, the same cannot be said for the very high currents sustained in the presence of excess sodium hydroxide. These latter data provide no evidence for the adsorption mechanism, but do show that phenol can be oxidised electrochemically, although, in this case, to produce a discontinuous, non-insulating film.

The scanning electron micrographs confirm these views. Where thicker films form (in the presence of excess sodium hydroxide or at  $850\text{mV}$  in the equimolar phenol/sodium hydroxide solution) they have lateral weaknesses that produce cracking related to the topography of the substrate. These films would be expected to have a limited ability to hinder electrochemical reactions, particularly when they form in the presence of a compound that provides an additional electroactive species. The micrographs also provide strong evidence for the formation of an extremely thin insulating layer in the presence of equimolar phenol/sodium hydroxide at the higher potential or excess phenol. At both potentials, taken as joint evidence with the electrochemical results, it appears that the thin films do not suffer from the poor cohesion of the thick films, since the currents fall to very low values. Impedance measurements are now in hand to establish the properties of these films more fully.

## Conclusions

The data reported here shows that under specific conditions of solution composition and electrode potential, mild steel can be coated with a continuous and insulating film by anodic polarisation in a phenol/sodium hydroxide solution. This film has the characteristics of some anodic films formed from the metal in that its formation is able to stifle its own growth and, when continuous, hinders other electrochemical reactions, such as oxygen evolution. The anodic film formed, however, is derived from the solution not the metal in this case. It appears, therefore, that the technique described might form the basis of a protective coating method for iron and mild steel. At this stage, no attempt has been made to establish the corrosion resistance conferred on the steel by the coating, nor has the possibility of coating other metals by the same technique been investigated. The thicker films that form have been shown to have mechanical deficiencies that produce holidays in the coating; the coherent films are extremely thin. In this context it may be that a substituted phenol might prove a better starting point for polymerisation if it introduced the possibility of strengthening the coating by crosslinking, yet enabled a thicker coating to be applied.

## Acknowledgment

The authors wish to thank Professor G. C. Wood for the provision of laboratory facilities.

[Received 8 November 1977

**References**

1. Mayne, J. E. O., "Corrosion" (Shreir, L. L., Ed.), *Newnes-Butterworths* 15.3, London and Boston (1976).
2. Mayne, J. E. O., *Br. Corros. J.*, 1970, **5**, 106.
3. Brockman, R. J., *Electroorganic Chemistry*, Wiley, New York, 1926.
4. Vijn, A. K. and Conway, B. E., *Chem. Rev.*, 1967, **67**, 623.
5. Fleischmann, M. and Pletcher, D., *Chem. Brit.* 1975, **11**, 50.
6. Pickett, D. J. and Akhavan-Alizadeh, E., *J. Appl. Chem. Biotechnol.*, 1974, **24**, 63.
7. Wawzonek, S. and McIntyre, T. W., *J. Electrochem. Soc.*, 1967, **114**, 1025.
8. Mieluch, J., Sadkowski, A., Wild, J. and Zoltowski, P., *Przemysl Chemiczny*, 1975, **54**, 513.
9. Dijkstra, R. and De Jonge, J., "Science and technology of surface coatings" (Chapman, B. N. and Anderson, J. C., Eds.), *Academic Press*, London and New York, 1974.
10. Shimizu, T., Kunuzi, A. and Nagaura, S., *Denki Kagaku*, 1975, **43**, 269.
11. Prater, K. B., *J. Electrochem. Soc.*, 1973, **120**, 365.
12. Bejerano, T., Forgacs, Ch. and Gileadi, E., *J. Electroanal. Chem.*, 1970, **27**, 69.
13. Zeigerson, E. and Gileadi, E., *ibid*, 1970, **28**, 421.
14. Bejerano, T. and Gileadi, E., *ibid*, 1972, **38**, 137.



# Molecular weight fractionation experiments with alkyds

By J. D. Frazee

Materials and Tests Division, State Department of Highways and Public Transportation, Austin, Texas 78703, USA

## Summary

Several effects in fractionated alkyds are described including crystallinity, infrared spectra differences, and X-ray diffraction patterns. Aromatic chain stoppers appear to account for the infrared

spectral changes in the 1580-1600 $\text{cm}^{-1}$  range. Fractionation is a useful tool in studying the kinetics of alkyd production.

## Keywords

Raw materials for coatings  
binders (resins, etc.)  
alkyd resin

Properties, characteristics and conditions primarily associated with materials in general  
molecular weight

Processes and methods primarily associated with manufacturing or synthesis  
fractionation

## Des expériences de fractionation par poids moléculaire sur des résines alkydes

### Résumé

On décrit divers aspects des alkydes fractionnées, tels que la cristallinité, les différences à l'infra rouge, et les diagrammes de rayons X. Il semble que les rompeurs de chaîne aromatiques sont

responsables pour les changements à l'infra rouge dans l'intervalle de 1580 à 1600 cm. La fractionation est une technique utile pour étudier la cinétique de la production des résines alkydes.

## Molekulargewichts - Fraktionierung von Alkyden

### Zusammenfassung

Eine Anzahl von bemerkenswerten Beobachtungen an fraktionierten Alkyden, einschliesslich Kristallform, infrarote Unterschiede und Röntgenstrahlendiffraktionsmuster werden beschrieben. Aromatische Kettenstopper scheinen die Ursache für die Infrarotänder-

ungen im 1580-1600 $\text{cm}^{-1}$  Bereich zu sein. Fraktionierung ist ein für das Studium der Kinetik im Alkydherstellungsprozess nützliches Verfahren.

## Introduction

Ref. 1

In a previous article in this *Journal*, the author noted that a medium oil alkyd was obtained in crystalline form under particular conditions<sup>1</sup>. Several samples of traffic alkyd had been sent for gel permeation chromatography (GPC) analysis. The 5 ml GPC fractions had been collected in vials, stoppered, and stored undisturbed. Under these conditions, a few of the vials slowly lost their solvent, and the solid alkyd reformed under conditions ideal for polymer crystallisation to take place (dilute solution, slow evaporation, and narrow molecular weight range).

The vials were not examined until six weeks after storage. Several vials had lost their solvent. One vial in particular contained a matrix of amorphous alkyd and needle-like crystals (approximately 0.3 mm by 2 to 10 mm). This sample was microphotographed (see Figure 1) and briefly reported<sup>1</sup>.

Since GPC analysis is not normally available in the author's laboratory, it was decided to limit further study of this phenomena to more classical methods. Accordingly, numerous experiments have been done to investigate further fractionation of alkyds by solvent techniques. The present communication gives the results obtained so far in this continuing investigation.

## Solvent fractionation experiments

Several solvents have been tested for separating alkyds into molecular weight fractions. Both normal heptane and ethyl



Fig. 1. Drawing from a microphotograph of the narrow molecular weight fraction of the alkyd that is discussed in the text. Crystalline regions are marked C. Amorphous regions are marked A.

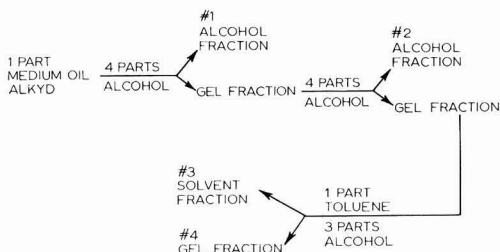


Fig. 2. Solvent separation of medium oil alkyd with absolute alcohol

alcohol are satisfactory. The scheme shown in Figure 2 separates medium oil alkyds into broad molecular weight fractions. The first mixture consists of the alkyd in its solvent (40 to 50 per cent toluene or VM&P naphtha) and 4 parts by volume of alcohol. The mixture is shaken vigorously for 10 minutes and then allowed to settle overnight. The soluble fraction is removed and the process is repeated on the gel fraction. In the case of the third and fourth fractions, the separating solvent is 1 part toluene and 3 parts alcohol. This yields four fractions which can be used to characterise the molecular weight spread of the sample. In a particular case, the distribution was:

Fraction #1	1.2ml
#2	0.8
#3	1.5
#4	2.5
Total	6.0

Considerable variation has been observed in the distribution of the medium oil alkyds so far tested. It appears that a fractionation procedure of this type could be useful in typifying alkyd resins. Greater reproducibility of the data could be obtained if the original sample was oven-dried and then toluene added, thus eliminating the variation in per cent and type of solvent.

### Crystallisation experiments

Ref. 6

Numerous attempts have been made to reproduce the results of the GPC experiment by solvent fractionation. Although samples have been divided into six or more fractions, no true crystals have been obtained by solvent methods.

The four fractions listed above vary in physical form as follows:

Fraction	Physical form
#1	Viscous liquid
#2	Highly viscous liquid
#3	
#4	Hard, sticky solid

In trying to obtain crystals from toluene solutions of the highest molecular weight fraction, the following sequence often occurs: The evaporation of the solvent produces strings of polymeric gel. Further evaporation causes the gel to accumulate as sheets, which frequently roll up like a rug presenting a fibre-like appearance (Figure 3). This sequence may show how true crystals are formed in the GPC fractions because the alkyd molecules should have a strong intermolecular attraction along the hydrocarbon oil axis. Also, it indicates that at least some of the low molecule weight fraction alkyd is needed as a plasticiser and dispersing agent for the alkyd resin.

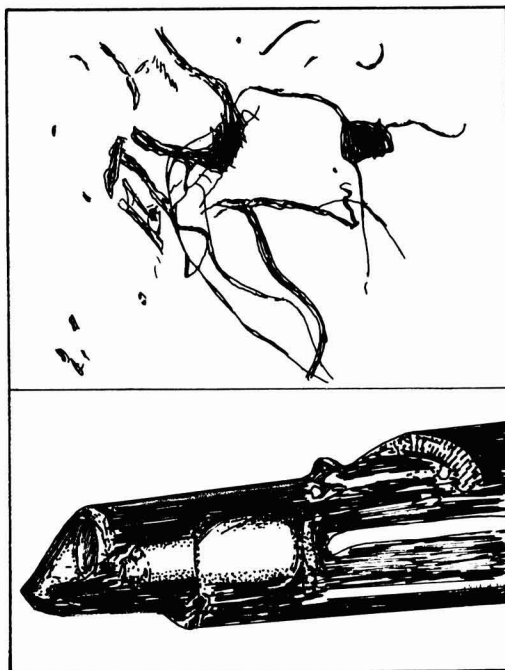


Fig. 3. Drawing from a microphotograph of strands of alkyd gel (above) and a closer up view of the rolled property

The fractions were examined by X-ray diffraction to determine if any submicroscopic order was present. The diffraction pattern of the whole alkyd (less solvent) and the alkyd fractions were essentially identical (Figure 4). The predominant peak occurred at  $19$  to  $21^\circ$  with a very broad, weak peak at  $40$  to  $42^\circ$ . This same curve was also obtained for cured alkyds. X-ray data were obtained for a variety of hydrocarbons. From a comparison with petroleum jelly and paraffin wax, it can be concluded that the  $21^\circ$  peak is associated with the  $\text{CH}_2$  unit (see Tables 1 and 2). The value of  $21.0^\circ$  can be compared to the handbook value of  $21.4^\circ$  for this principle line in paraffin wax<sup>6</sup>.

Table 1  
X-ray diffraction of medium oil alkyd (solvent removed)

Material	Diffraction Peak ( $2\theta^\circ$ )	Relative Peak Height	
A. Uncured whole alkyd	20	70	
	40	20	
B. Alkyd fraction No. 1	20	35	
	44	5	
	fraction No. 2	19	70
		42	7
	fraction No. 3	20	100
		40	7
	fraction No. 4	20	73
		44	10
C. Cured whole alkyd	20	30	
	41	5	

*Crosfield*  
**SILICAS**

**Consider where our other silicas are used  
before you use our matting agents.**





## **Crosfield Silicas. What we've done for others, we'll happily do for you.**

Crosfield matting agents do a very good job.

But when you consider what lies behind them, that's not really surprising. Over our 50 years in the business, we have developed a wide range of silicas to meet specific technical needs in industry.

They're used to protect aero engines in storage for instance. To clarify lager, anti-block packaging film and to thicken toothpaste.

It's this versatility that's put us at the forefront of silica technology – and has enabled us to create a range of matting agents that is second to none.

Above all, Crosfield HP Silicas\* offer excellent matting efficiency and achieve the required effect with exceptional economy.

They give you outstanding clarity and a superb film smoothness like silk.

They can readily be incorporated by standard high speed dispersion techniques and give good mar resistance to the finished product.

All of which should make one thing clear.

Crosfield HP Silica matting agents can help you, just as our other silicas have helped other people to make better products.

\* "Crosfield HP" is a proprietary brand name.

***Crosfield***  
**SILICAS**

**experience tells in the end**

JOSEPH CROSFIELD & SONS, LIMITED, P.O. BOX 26, WARRINGTON, CHESHIRE, UK, WA5 1AB  
Telephone: Warrington (0925) 31211. Telex: 627067

Table 2  
X-ray diffraction of hydrocarbon films<sup>5</sup>

Material	Absorption peak 2θ (degrees)	Relative peak height	Description*
White petroleum jelly (Vaseline)	18	48	Sh
	18.7	47	Sh
	21	37	Sh
	23.5	18	Sh
	40	5	Br
Phenoxy resin (Bakelite PKHH)	24	19	Br
	44	2	VBr
Methacrylate resin (R and H B66)	18	30	
	30	8	Br
Rubber cement (Carter Co.)	20	20	
	40	10	VBr
Pressure sensitive tape (3M Co. No. 102)	20	15	
	43	7	
Latex rubber (Perry 366)	24	21	Br
	40.5	19	Br
Medium oil alkyd (100%, uncured)	20.3	90	Br
	41	40	Br
Cured rubber	30.3	100	Sh
	29.5	60	Sh
	10.3	60	Sh
Polyurethane resin	20.1	49	Br
	41.5	20	Br
Vinyl toluene/acrylate	19.3	27	Br
	41.6	10	Br
Silicone modified alkyd (Cargill)	19.3	41	Br
	40.0	20	Br
Linseed oil, modified (Archer D. M.)	19	135	Br
	41	37	Br
Long oil alkyd (100%)	20	57	Br
	41.3	36	Br
Paraffin wax (Gulf Oil Co.)	21.0	100	Sh
	23.35	50	Sh
	29.5	4	Sh
	35.6	5	Sh
	39.8	12	Sh
	42.2	14	Sh
	44.6	10	Sh
47.0	2	Sh	

\*Sh = Sharp

Br = Broad

VBr = Very Broad

Other samples of alkyd were examined for diffraction peaks. This included:

(a) A sample of alkyd without stabiliser that had set in storage for four years and formed a tough gel.

(b) A sample of chlorinated rubber-alkyd traffic paint that was two weeks old and a sample taken after long-term field service. The resins were extracted with hot toluene.

(c) A sample of cured alkyd film stretched 80 per cent. The stretch lines could be observed in this sample with a microscope.

All of these samples gave essentially the same X-ray scans as those shown in Figure 4. Relative variations in the peaks at 21° and 42° did not follow a simple pattern and no other peaks were observed.

The general alkyd peak at 21° is strong, but not sharp. It may actually consist of two peaks of near equal intensity, the 21° peak and a peak at about 18.5°.

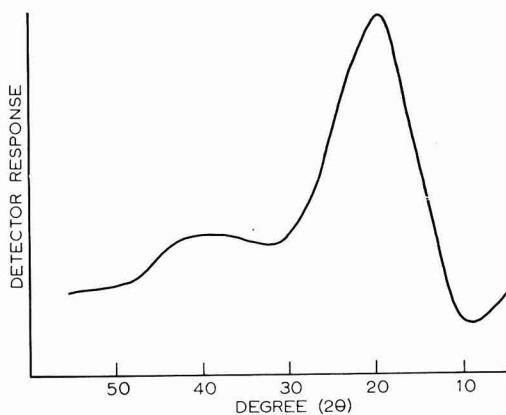


Fig. 4. X-ray diffraction pattern of alkyds and alkyd fractions

### Infrared experiments

Ref. 2

The infrared spectra of alkyd fractions were examined to compare the hydroxyl content, methylene content, and carbonyl content. The typifying peaks for each group are:

OH: 3500cm<sup>-1</sup>

CH<sub>2</sub>: 2920cm<sup>-1</sup>

CO: 1730cm<sup>-1</sup>

Table 3 gives typical data for the relative peak heights for the four fractions listed in Table 1. The high molecular weight fraction has the largest relative percentage of hydroxyl groups. This is in agreement with the extensive work of Walz on pentaerythritol alkyds<sup>2</sup>. However, further work will be required in order to elucidate the reaction mechanisms of glycerol, fatty acid, alkyds as related to molecular weight. Walz emphasised the importance of linear molecules versus ring compounds to explain the increase in hydroxyl number at high molecular weights in pentaerythritol alkyds.

Table 3  
Relative infrared peak heights for alkyd fractions

Alkyd fraction	Infrared peak (cm <sup>-1</sup> )		
	3470	2920	1730
1	21	59	60
2	36	77	75
3	24	84	83
4	21	21	16
Original sample	33	84	85

### The aromatic peaks

Refs. 3, 4

An interesting aspect of the solvent fractionation experiments is the change in the peaks at 1600 and 1580 cm<sup>-1</sup>. These peaks are associated with aromatic, double-bond carbon stretching<sup>3</sup>. In the case of the terephthalic acid the 1580 cm<sup>-1</sup> absorption is stronger than 1600 cm<sup>-1</sup>. For the isophthalic acid (the *meta* isomer), the reverse is true, whilst the *ortho* isomer is inter-

mediate between these two<sup>4</sup>. Most substituted benzene rings exhibit an absorption band or bands near  $1600\text{ cm}^{-1}$ . This includes chain stoppers such as substituted benzoic acids. Toluene, an often used alkyd solvent, has a medium strong absorption band at  $1600\text{ cm}^{-1}$ .

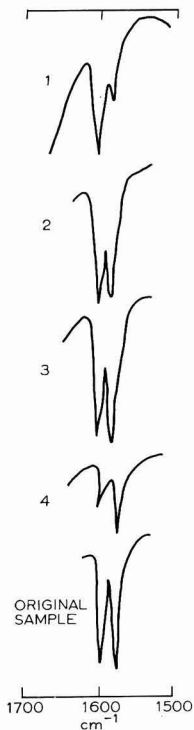


Fig. 5. Variation in the absorption peaks at  $1600$  and  $1580\text{ cm}^{-1}$  of alkyd fractions compared to the original sample. The average molecular weight of the fractions increases from fraction number one to number four.

Figure 5 shows that the relative strength of the absorption peaks at  $1600$  and  $1580\text{ cm}^{-1}$  for the lowest molecular weight fraction differs from the original sample. Also, the relative absorptions of these two peaks vary uniformly from the lowest to the highest molecular weight fraction.

Several explanations could be offered for this effect, such as isomerisation of the phthalic acid during the alkyd cook, toluene impurity in the infrared sample, or the presence of an aromatic chain stopper in the alkyd.

The trend of the results from fraction to fraction tends to rule out isomerisation as a major factor.

Tests have been conducted to date rule out toluene as the changing factor.

The phthalic anhydride alkyds used in this study came from several commercial sources. If it is assumed that aromatic chain stoppers were used in the cooks, then the lower molecular weight fractions might be expected to contain a larger percentage of chain stopper. This could account for the variation in the relative peak heights. For example, *para*-tertiarybutylbenzoic acid is often used as a chain stopper, and it has a strong absorption band<sup>4</sup> at  $1600\text{ cm}^{-1}$ .

Further support for this interpretation comes from the fact that ethanol extracts of cured alkyd samples gave scans similar to fraction number one. The unextracted portion gave a scan more like fraction three or four.

## Conclusions

Although alkyds have been available commercially for over forty years, much remains to be learned about the mechanisms by which alkyds are produced. Fractionation of alkyds and subsequent further analysis offers a fruitful approach to this problem area.

[Received 24 September 1977]

## References

1. Frazee, J. D., *JOCCA*, 1974, **57**, 308.
2. Walz, G., *JOCCA*, 1977, **60**, 11.
3. Afremow, L. C., et al, Chicago Society for Paint Technology, *FSCT*, Philadelphia, Pa., 1969.
4. Hummel, D. O., "Infrared Analysis of Polymers, Resins, and Additives An Atlas", *Wiley-Interscience*, New York, 1969.
5. All X-ray spectra were obtained on a Philips XRG-3000 instrument at 35 kilovolts and 12 milliamps. Film thicknesses were not closely controlled.
6. Berry, L. G. (editor), "Powder diffraction file search manual, organic, 1973". Publication SMO-23 of Joint Committee on Powder Diffraction Standards, Swarthmore, Pa., 1973.

# Mechanisms of efflorescence resistance in paint films

By J. Boxall

Department of the Environment, Building Research Establishment Princes Risborough, Aylesbury, Bucks HP17 9PX

## Summary

A range of laboratory prepared and proprietary paint coatings have been tested for their resistance to efflorescence. The coatings were applied to gypsum plaster panels which had been impregnated with sodium sulphate and then exposed to a source of water.

Efflorescence resistance of paints based on solvent-soluble polymers appeared to be distinguished by a low permeability and the pro-

vision of a uniform surface film on the plaster. Failure to meet these requirements, either by over pigmentation or excessive penetration resulted in loss of resistance. Paints based on emulsion polymers did not appear to be suitable binders for efflorescence resisting coatings, although the exact reason was not evident from this work.

## Keywords

### *Types and classes of coatings and allied products*

architectural finish  
masonry finish  
house paint

### *Types and classes of structures or surfaces to be coated*

gypsum plaster

### *Raw materials for coatings binders (resins, etc.)*

chlorinated rubber  
epoxy resin  
alkyd resin  
acrylic resin  
hydrocarbon resin  
urethane resin  
acrylic emulsion  
polyvinyl acetate resin  
styrene resin  
emulsion resin

### *prime pigments and dyes*

red iron oxide pigment

### *Properties, characteristics and conditions primarily associated with structures or surfaces to be coated*

efflorescence

dried or cured films

permeability

## Les mécanismes de résistance à l'efflorescence des films de peintures

### Résumé

On a essayé, au point de vue de la résistance à l'efflorescence, une série de peintures, et de commerce et préparées au laboratoire. Les peintures étaient appliquées aux panneaux de plâtre de gypse, qui avaient été imprégnés préalablement de sulfate de soude, et puis ils ont été exposés à l'eau.

La résistance à l'efflorescence des peintures basées sur des polymères solubles en solvants semblait d'exiger qu'elles ont une

faible perméabilité et aussi une aptitude à fournir une couche uniforme sur la surface du plâtre. Où la peinture ne répondait pas à ces exigences, à cause soit de surpigmentation, soit de pénétration excessive, il y avait une perte de résistance. Les peintures à base des émulsions polymères ne semblaient pas convenables en tant que liants pour revêtements résistants à l'efflorescence, bien que la raison précise ne fût pas mettre en évidence par la présent étude.

## Der Mechanismus von Widerstand gegen Ausblühung in Anstrichfilmen

### Zusammenfassung

Es wurde eine Anzahl von im Laboratorium hergestellten und im Handel befindlichen (Marken-) Anstrichmitteln auf ihre Widerstandskraft gegen Ausblühen geprüft. Die Anstrichfarben wurden auf Gipsstucktafeln, welche mit Natrium-sulfat imprägniert und darauf einem Wasserzufluss ausgesetzt worden waren, gestrichen.

Der Widerstand gegen Ausblühen von Farben auf Basis von in Lösungsmitteln löslichen Polymeren schien sich durch niedrige

Durchlässigkeit und die Bildung eines einheitlichen Films über dem Gipsstuck zu unterscheiden. Mangel an diesen Erfordernissen entweder durch Überpigmentierung oder übermäßiges Eindringen ergab Verlust des Widerstandes. Scheinbar sind Austrichmittel auf Emulsionspolymer-Basis ungeeignet für Zwecke der Ausblühverhinderung; allerdings ist die genaue Ursache durch diese Arbeit nicht nachgewiesen worden.

## Introduction

Refs. 1-4

The problem of efflorescence damage to paint coatings is associated with the presence within the substrate of water-soluble inorganic salts. The salt involved can be of various types depending on the substrate painted.

On concrete and other cementitious surfaces, calcium hydroxide, liberated by hydration of the cement, can migrate to the surface where evaporation of water and subsequent carbonation of the salt occur. This particular deposit is referred to as "lime-bloom".

The salt deposited on the surface of gypsum plasters is

essentially sodium sulphate, and the formation is again attributable to a drying-out process. The salt contamination in plasters can arise in a number of ways, but most commonly by either migration of soluble salts from adjacent concrete or brickwork, or from impurities contained within the plaster itself.

Both of these deposits, although differing in composition, are commonly referred to as "efflorescence", although in the work reported here the term is used to indicate sodium sulphate crystals. Discussions with building contractors<sup>1</sup> have confirmed that, whenever white crystals on plaster walls have been analysed, a large proportion of sodium sulphate has been present. Furthermore, paint failures on concrete attributable to the lime-bloom form of efflorescence seem to be comparatively rare in the UK.

Various ways of reducing paint failures due to efflorescence on plaster are possible, of which the most effective is to allow the substrate to dry out completely before beginning painting operations. Any efflorescent salts present are then clearly evident on the surface and can be brushed off prior to painting. However, the pressure to ensure building completion often makes it necessary for the plaster to be painted whilst still damp, when it is impossible to judge whether or not there is any risk of efflorescence. Under these circumstances it is customary to apply an emulsion paint formulated at a high pigment-volume-concentration in order that the salt in solution can permeate through the coating and crystallise on the surface without causing any disruption. However, this high pigment loading requirement can result in a coating that is inadequate in terms of other performance criteria, for example, mar resistance and washability. Such systems might, therefore, be considered as "holding" paints, to be replaced at a later date with more technically suitable coatings giving better performance in service.

An alternative approach involves treating the plaster in its damp condition with a coat of a plaster-primer or sealer before application of conventional decorative coatings. This approach is often adopted as a maintenance procedure on surfaces that have previously been affected by efflorescence, although there seems to be no conclusive evidence of the relative efficacy of this treatment.

The work reported here is part of a programme of work undertaken by the Princes Risborough Laboratory of the Building Research Establishment to investigate the tolerance of paint systems to adverse conditions and also to identify ways of improving performance. The problems associated with painting timber under adverse weather<sup>2</sup> and surface conditions<sup>3</sup>, and a summary of the experimental work on substrates other than wood have been reported elsewhere<sup>4</sup>. The present investigation was designed to determine the operative factors in the efflorescence resistance of paint coatings. This investigation involved the accelerated testing of a wide range of coatings on plaster panels impregnated with sodium sulphate to determine their resistance to efflorescence. Permeability studies of the coatings applied to plaster were also carried out.

## Experimental

### *Ref. 5*

### Paints and polymers evaluated

The polymers used in this investigation were chosen to cover as wide a range of types as possible, even though some of

these would not necessarily be used in paints for plaster substrates. Conventional techniques were used in the preparation of all the polymer and paint systems, although space necessitates that only a brief formulation outline is presented here. The commercial paints studied, however, were all specifically recommended for use on plaster substrates.

The systems evaluated are shown in Table 1. For convenience these have been sub-divided into unpigmented and pigmented solvent-soluble polymers, unpigmented and pigmented emulsion polymers and commercial products. Although not shown in the Table, each of the unpigmented emulsion polymers were also studied when modified with a cellulosic thickener of the ethyl hydroxyl ethyl cellulose type. An addition rate of 0.5 per cent thickener on the solids content of the emulsion was adopted and for this part of the study the solids content of the system was reduced from 50 to 25 per cent by weight. This simulated the probable condition of the polymer when used in a conventional emulsion paint type of formulations.

### Efflorescence testing

#### *Panel preparation*

Plaster panels, 200 × 130 × 13mm, were prepared using a two coat technique. A base coat comprising a mix of a retarded hemi-hydrate gypsum plaster conforming to British Standards 1191:1973 Gypsum Building Plasters, Part 1, Class B<sup>5</sup>, and tap water in the weight ratio of 3:1, was tamped into a wooden mould to a thickness of 10mm. After mechanically roughening the surface, the plaster was allowed to set for 24 hours at 20°C and 65 per cent relative humidity. A finishing coat, composed of the same plaster as used for the base coat and tap water in the weight ratio of 2:1, was then trowelled over the base to produce a finished thickness of 13mm. Predamping of the base coat was necessary prior to finishing in order to avoid excessive suction.

When the finishing coat had acquired a reasonable hardness, typically 2-3 hours after application, the surface of the panel was polished using a steel trowel, washed with deionised water, then left to dry at 20°C and 65 per cent relative humidity for 6 days. At some convenient time during this period the moulds were struck.

#### *Application of coating systems*

After the drying period, the test panels were immersed in a 2.5 per cent solution of sodium sulphate for 2.5 hours. This immersion period resulted in a salt solution uptake of 13-14 per cent of the initial panel weight (representing a dry salt loading of *ca* 0.4 per cent by weight). The saturated panels were then conditioned at 90 per cent relative humidity for 20 hours prior to painting.

The liquid loading of the test panels at the time of application was approximately 3-3.5 per cent of the initial dry panel weight, and this served to reduce penetration of the first coat of the applied paints and polymers to a realistic level, as well as adding to the severity of the testing.

All the paints and polymers were applied by brush to the finishing coat face of the test panels, with the necessary recoating being carried out over a period of two working days. All painting was performed at 20°C and 65 per cent relative humidity. After painting, the panels were stored at



Table 1  
Polymers and paints tested

Number	System	Formulation details		
		Ratio	% PVC	% Solids
<i>Solvent-soluble: unpigmented</i>				
1	Chlorinated rubber: chlorinated paraffin	1.0:0.6	—	40
2	Epoxy resin: polyamide	1.0:0.5	—	50
3	Alkyd, long oil length, linseed	—	—	50
4	Hydrocarbon resin	—	—	40
5	Acrylic resin, thermoplastic type	—	—	40
6	Polyurethane, moisture cured	—	—	40
<i>Solvent-soluble: pigmented</i>				
7	Chlorinated rubber: chlorinated paraffin	1.0:0.6	—	—
	Red iron oxide	—	40	50
8	Chlorinated rubber: chlorinated paraffin	1.0:0.6	—	—
	Red iron oxide	—	20	50
9	Chlorinated rubber: chlorinated paraffin	1.0:0.6	—	—
	Red iron oxide	—	10	50
10	Chlorinated rubber: chlorinated paraffin	1.0:0.6	—	—
	Red iron oxide: mica	1.0:1.0	20	50
11	Chlorinated rubber: chlorinated paraffin	0.6:1.0	—	—
	Red iron oxide	—	20	50
12	Chlorinated rubber: chlorinated paraffin	0.6:1.0	—	—
	Red iron oxide: mica	1.0:1.0	20	50
13	Higher viscosity variant of No 8	—	20	50
<i>Emulsions: unpigmented</i>				
14	Acrylic, 100% type	—	—	50
15	Polyvinyl acetate—Veova copolymer	75:25	—	50
16	Polyvinyl acetate—2 ethyl hexyl acrylate copolymer	—	—	50
17	Polyvinylidene chloride	—	—	50
18	Styrene acrylic copolymer	—	—	50
<i>Emulsions: pigmented</i>				
19	Styrene acrylic copolymer	—	—	—
	Red iron oxide	—	40	51
20	Styrene acrylic copolymer	—	—	—
	Red iron oxide	—	20	51
<i>Commercial products: primers-sealers</i>				
21	Pigmented chlorinated rubber	—	15	48
22	Hydrocarbon resin solution, unpigmented	—	—	32
23	Pigmented varnish. Def Stan 80-17/1	—	28	66
<i>Commercial products: finishes</i>				
24	Alkyd eggshell, white	—	34	70
25	Polyvinyl acetate copolymer emulsion, white	—	49	55
26	Polyvinyl acetate copolymer emulsion, white	—	36	53

these conditions for a further 5 days, and, immediately prior to testing, the edges were cleaned of dried salt and coated with a soft wax.

#### Testing

Testing for efflorescence resistance was performed by immersing the backs of the panels in deionised water for 5 days, after which time the panels were removed and left to dry for 3 days.

The test faces were then assessed for salt eruption through the film and for blistering, these being the only modes of failure observed throughout the testing. A rating system of 0-2 in intervals of 0.5 was used to assess performance. With this system 0 represented no failure and 2 severe failure.

Triplicate panels were used throughout the testing programme and the correlation was considered good. The results are shown in Table 2.

#### Permeability testing

##### Panel preparation

Panels for testing permeability were prepared by casting a 3:1 by weight mix of the retarded hemi-hydrate gypsum plaster and tap water into circular perspex moulds, 90mm diameter and 8mm thick. The degree of trowelling of the surface was maintained at a level consistent with the provision of an even compaction and a smooth finish.

The plaster was then allowed to set for 4 days at 20°C and 65 per cent relative humidity, prior to removal of the mould; after this drying was continued for a further 3 days.

##### Application of coating systems

After drying, the panels were immersed in a 2.5 per cent solution of sodium sulphate for 2.5 hours. After removal of the panels from the salt solution they were stored at 90 per cent relative humidity for 20 hours prior to painting. The

Table 2  
Test results

Number	System	Number of coats	Efflorescence resistance		Permeability gm <sup>2</sup> /24h
			Salt eruption	blistering	
<i>Solvent-soluble: unpigmented</i>					
1	Chlorinated rubber	2	0.5	0	22
2	Epoxy, 2 pack	2	0	0	25
3	Alkyd	2	0.5	0	34
4	Hydrocarbon	2	2	0	50
5	Acrylic	2	0.5	0	41
6	Polyurethane	2	0.5	0	34
<i>Solvent-soluble: pigmented</i>					
7	Chlorinated rubber 40% PVC	2	2	0	250
8	Chlorinated rubber 20% PVC	2	2	0	115
9	Chlorinated rubber 10% PVC	2	0.5	0.5	11
10	Pigment modification	2	1.5	0	91
11	Resin modification	2	1	0	117
12	Pigment and resin modification	2	1.5	0	183
13	Higher viscosity variant of No 8	2	0.5	0	93
<i>Emulsion: unpigmented</i>					
14	Acrylic	2	0.5	0.5	105
		4	0	0.5	
	Acrylic + cellulose addition	4	0.5	1	
15	PVA-Veova	2	0.5	0.5	68
		4	0	0	
	PVA-Veova + cellulose addition	4	1.5	0.5	
16	PVA-2EHA	2	0.5	2	65
		4	0	2	
	PVA-2EHA + cellulose addition	4	0.5	0.5	
17	PVDC	2	1	0	74
		4	1.5	0	
	PVDC + cellulose addition	4	2	0	
18	Styrene acrylic	2	1.5	2	22
	Styrene acrylic + cellulose addition	4	0	2	
		4	0	2	
<i>Emulsions: pigmented</i>					
19	Styrene acrylic 40% PVC	2	1.5	0	206
20	Styrene acrylic 20% PVC	2	1.5	1	72
<i>Commercial products:</i>					
<i>primers-sealers</i>					
21	Pigmented chlorinated rubber	1	0	0	22
22	Hydrocarbon sealer	1	2	0	115
23	Primer Def Stan 80-17/1	1	0.5	0	35
<i>Commercial products: finishes</i>					
24	Alkyd egg shell	2	0.5	0	32
25	PVA emulsion 49% PVC	2	2	2	178
26	PVA emulsion 36% PVC	2	2	2	103

salt loading of these permeability panels was similar to those of the panels for efflorescence testing.

The paint and polymer systems were applied following a similar procedure to that adopted for the preparation of the test panels for efflorescence resistance. After application of the systems, the test panels were allowed to dry for a further 4 days at 20°C and 65 per cent relative humidity prior to testing.

#### Permeability measurement

The permeability of the panels was measured using a cup technique with the plaster panels mounted, painted face uppermost, in aluminium dishes. A small quantity of water was placed in the cup before sealing the plaster test panel in position using a low melting point wax. After sealing, the cups were placed in a desiccator containing phosphorous pentoxide and weighings were performed periodically.

The surface area of the test panels after sealing was 50cm<sup>2</sup>, and all testing was performed in triplicate. There was very little variability between the replication of the results and only the arithmetic means are shown in Table 2, expressed as grams of water vapour transmitted through 1m<sup>2</sup> of film in 24 hours.

## Results

### Efflorescence resistance

#### Unpigmented solvent-soluble polymers

The best efflorescence resistance amongst the polymers in this group was exhibited by the two-pack epoxy, system 2, which exhibited no salt eruption after testing. The chlorinated rubber, alkyd, acrylic and polyurethane (systems 1, 3, 5 and 6), however, did allow more salt through the film although,

on close inspection, this was found to have originated from small, isolated, defects in the film.

The hydrocarbon resin, system 4, which penetrated excessively into the panels during application and formed only a minimal and patchy surface film, had the lowest resistance of all of the solvent-soluble polymers. After testing, the surface of this system was completely covered by a heavy salt deposit.

#### *Pigmented solvent-soluble polymers*

The formulation studies on the chlorinated rubber coating produced varied results. Reducing the film pigment volume concentration (PVC) from 40 per cent down to 10 per cent (systems 7, 8 and 9) resulted in improved resistance to efflorescence, although at the intermediate PVC of 20 per cent, performance was similar to that of the 40 per cent PVC system. At the 10 per cent PVC level (system 9) film blistering was evident, although on average this was restricted to one very small blister on each of the three test panels.

Modifying the pigment composition (system 10) and the resin-plasticiser ratio (system 11), whilst maintaining a consistent 20 per cent PVC, did offer some improvement in film efflorescence resistance, with the resin modification having the greater resistance to salt eruption of the two systems. However, the 20 per cent PVC paint containing both modifications (system 12) offered little improved performance.

All of these systems appeared to deposit uniform films on application, without excessive penetration. System 13, however, which was the higher viscosity variant of system 8 (6.5 poise compared with 2.3 poise), did show markedly improved efflorescence resistance.

#### *Unpigmented emulsion polymers*

None of the emulsion polymers studied in their two-coat form exhibited resistance to efflorescence, and all except the polyvinylidene chloride emulsion (system 17) also showed varying degrees of film blistering. The film of system 17 exhibited a rivelled appearance and this was especially pronounced on the four-coat system.

The four-coat application of the emulsion produced, with the exception of system 17, an improvement in efflorescence resistance, although a pronounced reduction in film blistering occurred in only one instance, that of the PVA-Veova (system 15).

The films produced from the emulsion systems were uniform and did not appear to penetrate excessively. With all systems, brush drag was especially noticeable when applying the first coat.

Addition of cellulose thickener to the emulsion generally resulted in a similar level of performance to the two-coat unmodified emulsions, although system 18, the styrene acrylic, was not adversely affected and continued to exhibit a performance comparable to that of the four-coat unmodified emulsion. The addition of the cellulose ether appeared to have little effect on film blistering tendencies. With all cellulose modified emulsions, the brush drag that had been pronounced during application of the unmodified versions was not evident.

#### *Commercial products: finishes*

The two emulsion paints studied (systems 25 and 26) had very low efflorescence resistance and blistered excessively during test. The alkyd eggshell (system 24) performed in a satisfactory

manner, with the rating of 0.5 representing only one small area of salt eruption on one of the test panels.

#### **Permeability**

The permeabilities of the films to water vapour varied within very wide limits, and few well defined trends were evident. The unpigmented solvent-soluble polymers however, generally exhibited lower permeabilities than their unpigmented emulsion counterparts. Pigmentation had a pronounced effect on permeability irrespective of polymer group, i.e. whether solvent-soluble or emulsion, with higher pigment loadings resulting in higher permeability rates.

#### **Discussion**

The results obtained suggest that differing mechanisms of efflorescence resistance are operative within the broad groups of solvent-soluble and emulsion polymers.

#### **Solvent-soluble paints and polymers**

Within the solvent-soluble class, resistance appears to be dependent upon the provision of a low permeability system and, perhaps most importantly, an associated requirement to establish a uniform coating thickness over the plaster surface. Failure to satisfy these requirements results in coatings of low efflorescence resistance, as demonstrated by the hydrocarbon resin (system 4) which due to its excessive penetration failed to establish a uniform coating. Inspection of the panels of the system during testing clearly established that failure was initiated from the areas of low film build. Furthermore, with the chlorinated rubber, acrylic and polyurethane systems which gave a uniform coating but only attained the low rating of 0.5 for salt eruption, the efflorescence appeared to initiate at, and subsequently spread from, point-source defects in the film.

The permeability of all the unpigmented solvent-soluble polymers was generally lower than their emulsion counterparts and, although not well defined, a water vapour permeability of less than 40 gm<sup>2</sup>/24h would appear to be required before protection can be established with this class of polymer.

The pigmentation studies on the chlorinated rubber polymer suggest a similar mechanism of resistance. The results obtained by reducing system pigment volume concentration demonstrate that a decrease produces a concomitant reduction in film permeability. Although not well defined, a similar permeability requirement to that suggested by the results obtained for the unpigmented solvent-soluble polymers would appear likely.

Penetration and film build is also important. This is illustrated by the differences in efflorescence resistance when the 20 per cent PVC system (system 8) with a viscosity of 2.3 poise was increased in viscosity to 8.5 poise (system 13) with consequent improvement in results. Minor changes in the pigment type and resin-plasticiser ratio at a constant PVC (systems 10, 11 and 12) gave significant changes in the film permeability and, although some improvements in efflorescence resistance were achieved, by and large these were not as marked as the improvements achieved by modifying film PVC (systems 7, 8 and 9).

#### **Emulsion paints and polymers**

The mechanism of efflorescence resistance in the unpigmented emulsion polymers studied seems somewhat more complex.

The initial work on the five systems indicates that in their two-coat form, there are no examples of resistant types. The effect of increasing the film thickness was to increase the efflorescence resistance of all of the emulsions, except the polyvinylidene chloride type, and this finding tends to support those for the solvent-soluble systems. In the case of the emulsion systems, however, it seems probable that the improved performance was attributable to the corresponding decrease in film permeability with increasing thickness, since there was no evidence from any of the two-coat systems to suggest that penetration into the plaster had been excessive, or irregular.

The addition of cellulose thickener to the emulsions applied in the four-coat system, which was designed to simulate a more practical condition for emulsion usage, was generally found to decrease the efflorescence resistance of the film to that of the two-coat unmodified variant. The resistance of the styrene-acrylic system was not, however, adversely affected by modification with cellulose ether. The pronounced film blistering evident with many of the emulsions in both two- and four-coat systems, was not found with the solvent-soluble polymers, and this suggests a particular form of defect that might be characteristic of emulsions as a class. It is possible that the observed blistering of the emulsions is a function of adhesion, rather than of coating permeability, especially under wet conditions.

The limited pigmentation study of the styrene acrylic emulsion suggests that acceptable performance with emulsion paints is not readily achieved by using conventional formulating techniques, and this particular aspect will form the basis of further work. What is interesting from this result, however, is the observed degree of film disruption found with the high PVC paint (system 19). Despite the very high permeability of this system, there was no indication that salt transmission was facilitated and damage to the film during surface crystallisation of the salt was extensive.

### Commercial products

The results obtained for the commercial paints tend to support the above observations for solvent-soluble and emulsion systems.

All the primer-sealers evaluated were based on the solvent-soluble class of polymer, but adequate efflorescence resistance was exhibited only by the pigmented systems 21 and 23. Both of these primers had low permeabilities and, with the one-coat application recommended by the manufacturer, produced a uniform film showing no signs of excessive or uneven

penetration. In contrast, system 22, the unpigmented hydrocarbon resin sealer, did penetrate excessively and afforded no protection. Interestingly, although not recorded here, dilution of systems 21 and 23 was detrimental to their efflorescence resistance, and this could be related to the increased penetration into the plaster which results from such modification.

The two emulsion finishes (systems 25 and 26) had poor resistance to efflorescence and also exhibited pronounced blistering. The alkyd eggshell, however, which had a low permeability, demonstrated good film resistance.

### Conclusions

Within paints based on solvent-soluble resins, efflorescence resistance appears to be determined by low permeability and the provision of a uniform surface film. Failure to meet these requirements, as a result of either over-pigmentation or excessive penetration, results in a loss of resistance. This low permeability requirement would, however, retard the drying out of the plaster and it must be acknowledged that this could induce other types of paint problem, most notably the risk of blistering in systems with low adhesion under wet conditions.

Emulsion polymers do not appear to be suitable binders for efflorescence-resistant coatings, although the exact reason is not evident from this work. The test results obtained from some commercial primers and finishes for plaster tend to confirm the above observations drawn from the experimental systems.

This work has also suggested that the concept of formulating high pigment volume concentration paints that will allow permeation of salt without film disruption is not tenable. However, the application of a solvent-soluble primer to damp plaster prior to application of conventional (non-resistant) emulsion coatings does seem to be an effective treatment, although the primer would itself have to satisfy the above requirements for efflorescence resistance.

[Received 19 December 1977]

### References

1. *Private communications*. Hill, G. V., Paint Research Association, Teddington, Middlesex.
2. Boxall, J. *J.O.C.C.A.*, 1977, **60**, 43.
3. Boxall, J., *BRE Information Sheet* IS 20-77, 1977.
4. *DOE Construction*, 1975, **15**, 14.
5. *British Standard 1191: 1973* "Gypsum Building Plasters", Part 1. British Standards Institution.

# The photocatalytic oxidation of liquid phase propan-2-ol by pure rutile and titanium dioxide pigments

By R. B. Cundall\*, B. Hulme†, R. Rudham and M. S. Salim

\*Department of Chemistry, University of Salford, Salford M5 4WT

†Tioxide International Ltd, Stockton-on-Tees, Cleveland TS18 2QN

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

## Summary

The rate of photocatalytic oxidation of liquid propan-2-ol to acetone on a pure rutile titanium dioxide surface depends on the oxygen pressure, concentration of rutile in suspension, intensity of the incident UV radiation, and the amount of water present. These are the same factors that are important in natural weathering of paint films. A mechanism in which reactive species are formed by the trapping of photo-electrons and photo-holes at the oxide surface is discussed.

Rates of acetone formation on nine commercial TiO<sub>2</sub> pigments at 310K have been determined, and a well defined sequence of photo-activity was obtained from experiments of not more than 5 hours' duration. The activity sequence is closely similar to that obtained from seven of the pigments in conventional accelerated weathering tests on paint films. It is suggested that the photocatalytic oxidation of propan-2-ol could form the basis of a rapid method of assessing the photoactivity of TiO<sub>2</sub> pigments.

## Keywords

### Raw materials

#### prime pigments and dyes

anatase titanium dioxide  
rutile titanium dioxide

### Processes and methods primarily associated with analysis, measurement or testing

accelerated weathering  
accelerated testing

### service or utility

photo-oxidation  
photoactivation

### Properties, characteristics and conditions primarily associated with dried or cured films

chalking

### Miscellaneous terms

UV light

## L'oxydation photocatalytique de propan-2-ol en phase liquide par le rutile pur ou par des pigments du dioxyde de titane

### Résumé

La vitesse de l'oxydation photocatalytique, sur la surface du rutile pur, de propan-2-ol à acétone se dépend de la pression d'oxygène, de la concentration de rutile en suspension, de l'intensité de la radiation ultra-violet incidente, et de la quantité d'eau qui est présente. Celles-ci sont les mêmes facteurs qui exercent une influence importante sur le vieillissement de films de peintures. On discute un mécanisme où les espèces réactives sont formées par le captage de photo-électrons et de photolalunes à la surface de l'oxyde.

On a déterminé sur neuf pigments du dioxyde de titane de commerce les vitesses de formation d'acétone à 310 K, et on a obtenu une séquence de photo-activité bien définie, grâce aux expériences dont la durée ne dépasse pas cinq heures. La séquence d'activité est très semblable à celle que mettent en évidence les essais conventionnels de vieillissement accélérés effectués sur les films de peintures basés sur sept parmi les neuf pigments mentionnés. On suggère que l'oxydation photocatalytique de propan-2-ol pourrait constituer la base d'une méthode pour déterminer rapidement la photoactivité des pigments du dioxyde de titane.

## Die photokatalytische Oxidation von Propan-2-ol in flüssiger Phase durch reine, rutile und Titandioxidpigmente

### Zusammenfassung

Die Geschwindigkeit der photokatalytischen Oxidierung von flüssigem Propan-2-ol über einer Oberfläche von reinem rutilen Titandioxid zu Azeton ist abhängig vom Sauerstoffdruck, der Konzentration des Rutils in der Aufschwemmung, der Intensität der einfallenden UV-Bestrahlung und der anwesenden Wassermenge. Dieselben Faktoren sind für die natürliche Verwitterung von Anstrichfilmen wichtig. Ein Mechanismus wird besprochen, in dem reaktive Spezies durch Einfangen von Photoelektronen und Photolöcher an der Oxidoberfläche gebildet werden.

Es wurde die Zeitdauer für die Bildung von Azeton mit neun TiO<sub>2</sub> Pigmenten des Handels bei 310K bestimmt, und in nicht länger als 5 Std. dauernden Experimenten wurde eine klar definierte Reihenfolge der Photoaktivität erkannt. Letztere ähnelt sehr der bei konventionellen, künstlichen Bewitterungsversuchen mit sieben der Pigmente in Lackfilmen erhaltenen. Es wird vorgeschlagen, die photokatalytische Oxidation von Propandiol als Grundlage für eine schnelle Methode zur Bestimmung der Photoaktivität von TiO<sub>2</sub> Pigmenten zu verwenden.

## Introduction

### Refs. 1-11

The successful development of highly durable TiO<sub>2</sub> pigmented paints calls for reliable methods of accelerated testing. Numerous methods are available,<sup>1,2</sup> and these include direct

measurements of the photochemical activity of the TiO<sub>2</sub> pigment itself. Although such measurements possess the merits of ease and rapidity, experience has shown that the results do not correlate well with those obtained from the natural weathering of paint films. This is not surprising when it is realised that a number of the tests are conducted under

conditions where at least one of the factors important in natural weathering is absent. It is generally agreed that these factors are: the radiation which is absorbed by the pigment, an oxidisable medium, and the presence of both oxygen and water.

Following the observation by Goodeve and Kitchener<sup>3</sup> of the TiO<sub>2</sub> photosensitised bleaching of chlorazol sky-blue dye, colour changes in various organic dyestuffs have been used as a method of assessing photochemical activity<sup>4,5,6</sup>. Such methods are, however, adversely affected by atmospheric oxygen. The photocatalysed oxidation of relatively small organic molecules, usually in the absence of air, forms the basis of a number of photochemical tests<sup>6,7,8,9</sup>. Oxidation proceeds at the expense of lattice oxygen, and the formation of Ti<sup>3+</sup> ions can be detected by ESR<sup>9</sup> or optical methods<sup>6,7,8</sup>. Amongst the tests which can be conducted in the presence of air, the authors were impressed by Irick's observations of the photocatalytic oxidation of liquid propan-2-ol to acetone<sup>10</sup>. The reaction was capable of differentiating between the photoactivities of anatase, rutile and other white pigments, and a correlation was found between these activities and the rates of photodegradation of samples of pigmented polypropylene. In a previous publication<sup>11</sup> the authors have investigated the photocatalytic oxidation of liquid propan-2-ol, and have proposed a mechanism in which reactive species are formed by the trapping of both photo-electrons and photo-holes at the hydroxylated surface of pure rutile. It is the purpose of the present paper to confirm that the reaction requires the same conditions as does natural weathering of paint films, and to show that it is a sensitive method for determining the photoactivities of a number of commercial TiO<sub>2</sub> pigments.

## Experimental

*Ref. 12*

Irradiations were carried out in a cylindrical Pyrex vessel fitted with a helical stirrer, tubulations for atmosphere control, and a serum cap for extracting analytical samples by syringe. Experiments showed that a stirrer speed of 500rpm maintained the TiO<sub>2</sub> in suspension and gave reproducible results. Temperature control was achieved by mounting the vessel in a close fitting aluminium block containing channels, through which water from a thermostat was passed. The reaction vessel was located between two Mazda ME/D 250W medium pressure mercury arcs fitted with Pyrex filters. The radiation from each ( $\lambda > 316\text{nm}$ ), after passing through a heat filter of 10cm thickness of 2 molar acetic acid, was focussed on the vessel through a rectangular aperture in the aluminium block. The intensity of incident radiation from each source was monitored using fibre optics, a photocell and valve voltmeter.

After centrifuging, reaction mixture samples were analysed using a Pye-Unicam series 104 flame ionisation gas chromatograph with a 2.1m column of 10 per cent polyethylene glycol (MW 400) on Chromosorb W at 343K with N<sub>2</sub> carrier gas flowing at 1.6cm<sup>3</sup> s<sup>-1</sup>. Owing to the low concentration of acetone formed, an internal standard was essential if reproducible analyses were to be obtained; diethyl ether was selected since it was fully eluted before the acetone. Equal volumes of centrifuged reaction mixture and of a standard solution of diethyl ether in propan-2-ol were thoroughly mixed before injection of a 3 $\mu$ l sample. Since the chromatograph had previously been calibrated using varying concentrations of acetone and a fixed concentration of diethyl ether in propan-2-ol, the concentration of acetone in the reaction mixture was obtained from the ratio of the peak heights given by acetone and diethyl ether.

In addition to a sample of highly pure rutile, which has previously been described<sup>12</sup>, experiments were also made with the commercial pigments described in Table 1. Propan-2-ol and other reagents used were of analytical grade wherever possible.

## Results

### Experiments with pure rutile

*Refs. 11, 13-15*

A number of experiments have been made with pure rutile at 310K to determine the conditions necessary for the photocatalytic production of acetone. Unless stated otherwise, the reaction mixture consisted of 0.2g of rutile in 20cm<sup>3</sup> of propan-2-ol. No reaction product other than acetone could be detected by gas chromatography, although equivalent concentrations of water are probably produced. Plots of acetone concentration expressed in mol kg<sup>-1</sup> against time were found to be linear, so that the slope of such plots is accepted as the rate of reaction.

The effect of the partial pressure of oxygen on the rate of acetone production is shown in Figure 2(a). In these experiments, controlled flows of O<sub>2</sub> and N<sub>2</sub> were mixed, and a combined flow of 160cm<sup>3</sup> min<sup>-1</sup> was passed over the reaction mixture. In the presence of N<sub>2</sub> alone, the rutile became pale grey through reduction, but acetone production could not be detected. To maximise the rate of acetone production, all further experiments were conducted in pure oxygen.

The effect of varying the weight of rutile in 20cm<sup>3</sup> of propan-2-ol is shown in Figure 2(b). From a complete lack of reaction in the absence of rutile, the rate increases and

Table 1  
Details of pigments and their photoactivities for acetone formation

Pigment	Crystal structure	Area m <sup>2</sup> g <sup>-1</sup>	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	ZnO (%)	P <sub>2</sub> O <sub>5</sub> (%)	Organic surface treatment	10 <sup>6</sup> × rate of acetone formation/mol kg <sup>-1</sup> min <sup>-1</sup>
1	rutile	7.7	none	none	none	none	no	400
2	anatase	10.2	0.01	0.01	none	0.4	no	320
3	rutile	9.3	0.1	0.1	1.0	0.2	no	52
4	rutile	11.2	2.0	5.2	none	0.2	yes	41
5	rutile	13.7	4.3	3.6	none	none	yes	23
6	rutile	10.7	1.2	2.4	1.0	0.2	yes	17
7	rutile	10.4	2.1	4.2	none	0.1	no	14
8	rutile	15.8	0.8	3.2	1.0	0.2	yes	11
9	rutile	9.7	3.1	4.4	none	0.1	no	7
10	rutile	11.3	1.3	2.5	1.0	0.2	yes	4

# Paint with a great body.

Methocel\* methyl cellulose ether does so much for your latex paints and not just as a thickener but as a protective colloid and a pigment suspension aid.

You can see it in the finish: excellent brushability. Less sagging. Increased stability in the initial drying stages.

It simply makes a good paint great. And as Methocel has good resistance to enzyme attack it helps give paint a long shelf life. Let us prove it to you. Write for more details now.

Dow Chemical Company Ltd.

a) Heathrow House, Bath Road, Hounslow TW5 9QY, Tel. 759 2600

b) Grove Chambers, Green Lane, Wilmslow, Cheshire SK9 1LN, Tel. 27 131

c) Swan Office Centre, 1508 Coventry Road, Yardley, Birmingham B25 8AD, Tel. 021-707 2525

Please attach this coupon to your letter-heading, stating your name and send to one of the addresses above for further details of METHOCCEL.

**METHOCCEL\*** 

**Adds body to your paint**



\* Trademark of The Dow Chemical Company

# The Biggest





# Thing in Greens

Big things are happening to ICI's phthalocyanine green pigments. We're already world leaders in the green pigment market ... and now we're taking a giant step forward with a massive new £6 m plant. It's a huge development—designed to double our capacity to an annual total of 3000 tonnes.

Today, the Monastral range of phthalocyanine green pigments is of particular importance to the Automotive Paint Industry. Monastral Green pigments produce cleaner, brighter shades than any alternative ... and give excellent all-round fastness.

They're completely versatile and cover an entire spectrum of colours from bright yellowish-greens to bright bluish-greens. They also cover many grades to meet the requirements of all pigment users.

In fact, ICI's phthalocyanine greens are now used extensively for all types of paints, inks and plastics. And they're growing in popularity in other areas ... especially for the coloration of paper, textile printing compositions, viscose rayon, artist's paints, powder coatings, waterproof canvas, and for soaps and detergents too!

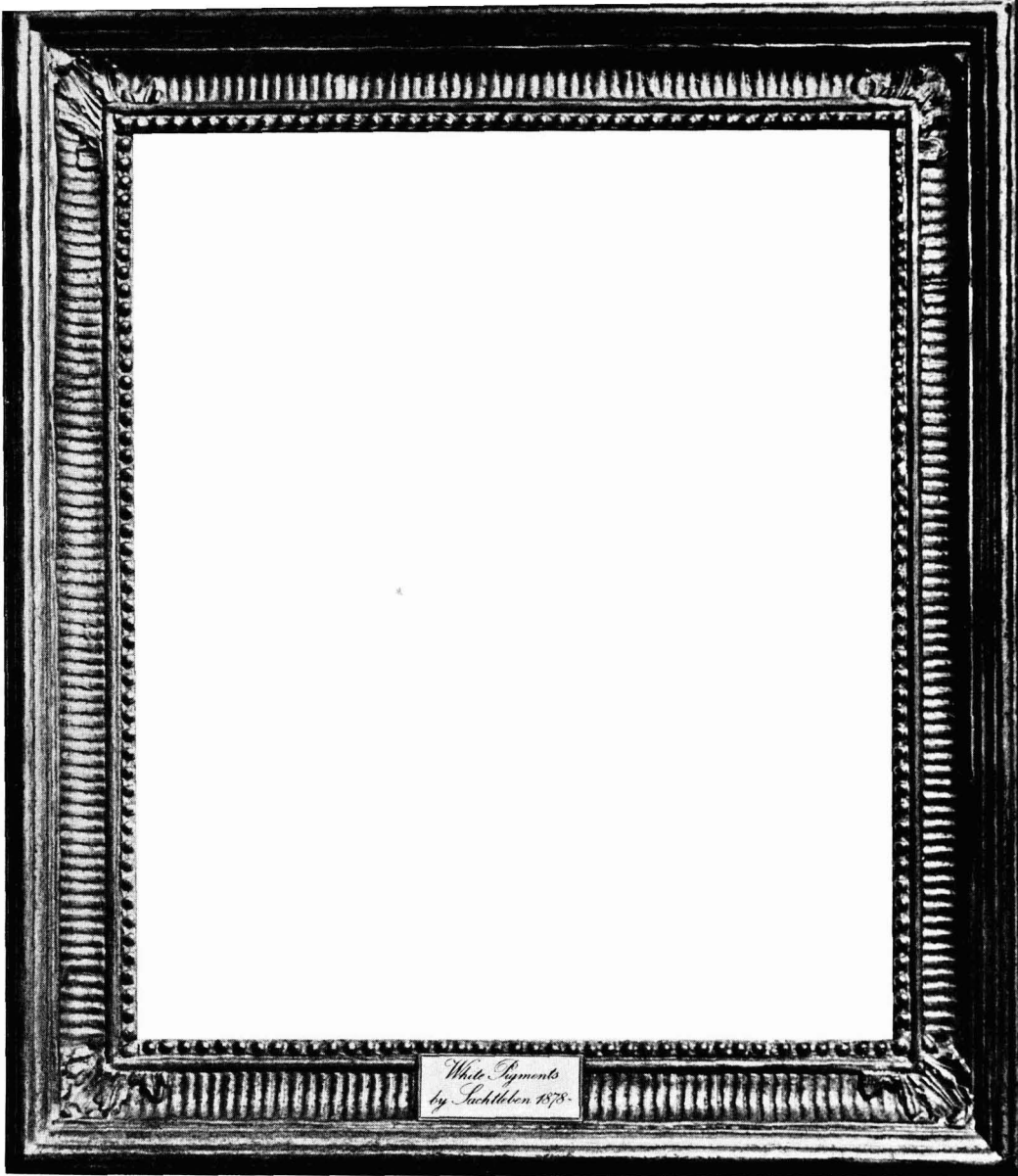
Things really are happening to phthalocyanine green pigments—the biggest thing in greens ... from ICI.



**Organics Division** 

Hexagon House, Blackley, Manchester M9 3DA

OD 142



Hombitan® Titanium Dioxide, a work of art and science. Our painting in white.

Consistently white pigments have been our claim to fame for a century.

Our paint pigments are produced in a number of grades for specific tasks:

**Hombitan R 511** is a universal pigment with extremely good optical efficiency and improved dispersibility for all types of paints.

**Hombitan R 506** is a special pigment for high loaded indoor paints. It has very high tint reduction, scattering power and good weather resistance.

**Hombitan R 210** is a pigment with very high scattering power for pure white industrial finishes and indoor uses, giving high gloss without hazing.

**Hombitan R 611** is universally applicable, easily dispersed and gives outstanding weather resistance to exterior finishes.

All Hombitan paint pigments are made in our own plant to strictly controlled standards and have a world-wide technical backing.

If you'd like to know more about our competitively priced, readily available Hombitan masterpieces, get in touch with our UK sales office by telephone, telex or letter.

They will be pleased to put you in the picture.



» **SACHTLEBEN** «

Chemie GmbH

D4100 Duisburg 17

UK Sales Office, 56 High Street,  
Edenbridge, Kent TN8 5AJ

Telephone (0732) 863694 Telex: 95297

Manufacturers of Hombitan® R 511, Hombitan® R 506, Hombitan® R 210, Hombitan® R 611.

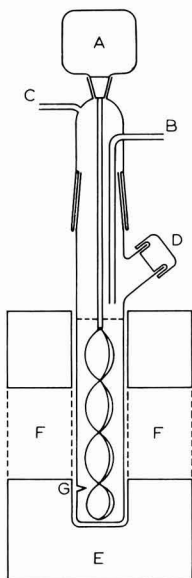


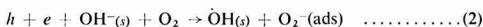
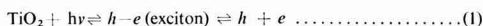
Fig. 1. The reaction vessel: A, micro stirrer motor; B, gas inlet; C, gas outlet; D, serum cap; E, aluminium block; F, irradiation aperture; G, thermocouple pocket

reaches a plateau in activity of  $5.0 \times 10^{-4} \text{ mol kg}^{-1} \text{ min}^{-1}$  at weights exceeding  $\sim 0.4\text{g}$ . The results emphasise the requirement of a constant weight of rutile if reproducible results are to be obtained.

By inserting neutral density filters in both beams it was shown that the rate of acetone formation was directly proportional to the intensity of incident radiation. Figure 2(c) shows that the plot of rate against intensity passes through zero, corresponding to the experimental observation that acetone was not formed at 310K in the absence of UV radiation.

The influence of water on acetone production at 313K is shown in Figure 2(d), where the rate is plotted against the mole fraction of propan-2-ol in propan-2-ol/water reaction mixtures. The rate of reaction was also determined using propan-2-ol which had been dried by standing over freshly dehydrated 4A molecular sieve. Accepting that water plays an essential role in reaction, the small decrease in rate from  $4.63 \times 10^{-4} \text{ mol kg}^{-1} \text{ min}^{-1}$  to  $4.56 \times 10^{-4} \text{ mol kg}^{-1} \text{ min}^{-1}$  after drying, suggests that rutile exposed to the atmosphere contributes sufficient water for reaction to proceed. However, the slope of Figure 2(d) at high propan-2-ol concentrations indicates that water produced using the normal reaction mixture has no appreciable autocatalytic effect.

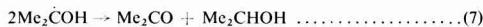
To account for the experimental observations the following mechanism is proposed<sup>11</sup>. Absorption of photons with energies greater than the band gap give rise to electrons and positive holes which are preferentially trapped at the hydroxylated rutile surface in the presence of oxygen<sup>13,14</sup>:



These reactions are followed by:



So that the  $\text{H}_2\text{O}$  produced in (3) regenerates  $\text{OH}^-(s)$  in (4), and the energy of the absorbed quantum is effectively utilised in producing  $\text{Me}_2\dot{\text{C}}\text{OH}$  and  $\dot{\text{H}}\text{O}_2$ . Formation of acetone from  $\text{Me}_2\dot{\text{C}}\text{OH}$  could occur in the following ways:



If reactions (6) and (7) occur,  $\text{H}_2\text{O}_2$  is formed by:



The  $\text{H}_2\text{O}_2$  from (5) or (8) takes no further part in the reaction unless it is decomposed by an additional photoelectron<sup>11</sup>. The effect of  $\text{H}_2\text{O}$  added to the reaction mixture will be to favour (4), but to inhibit (3) by non-fruitful interaction between  $\text{OH}(s)$  and  $\text{H}_2\text{O}$ . The results suggest that these opposing effects yield an optimum conditions at a propan-2-ol mole fraction of 0.3-0.4.

Quantum yields of  $\sim 0.38$ , using filtered radiation<sup>11</sup> at 366 and 404nm, are in agreement with such a mechanism rather than with a conventional radical chain mechanism. However, it is necessary to justify the assumption used in their calculation, that all incident radiation is absorbed. From a study of UV absorption between 320 and 400nm by  $\text{TiO}_2$  pigmented paint films, Hird<sup>15</sup> has shown that attenuation follows an exponential decay with thickness,  $I = I_0 \exp(-KX)$ , where  $I_0$  is the initial intensity inside the film,  $I$  is the intensity at depth  $X$ , and  $K$  is the attenuation constant. In addition to the usual wavelength dependence,  $K$  also depends upon the pigment volume concentration and particle size due to the interplay of absorption and scattering of the UV radiation. The authors have obtained values of  $K$  for a pigment volume concentration corresponding to 0.2g of rutile in  $20\text{cm}^3$  of propan-2-ol (0.235 per cent) by extrapolating plots of  $K/C$  against  $C$  for rutile possessing particle sizes similar to those used in the present work. Subsequent calculation showed that for wavelengths  $\leq 400\text{nm}$ , at least 99 per cent of the incident radiation is absorbed in 0.7mm of the reaction mixture. Since the experimental path length exceeded this by more than an order of magnitude, all incident radiation  $\leq 400\text{nm}$  is absorbed by the rutile in the standard reaction mixture. The position concerning wavelengths  $>400\text{nm}$  is less clear, but total absorption at 404nm is highly probable.

#### Experiments with commercial pigments

Refs. 16-17

Acetone production from 0.2g samples of nine commercial  $\text{TiO}_2$  pigments in  $20\text{cm}^3$  of propan-2-ol at 310K is shown in

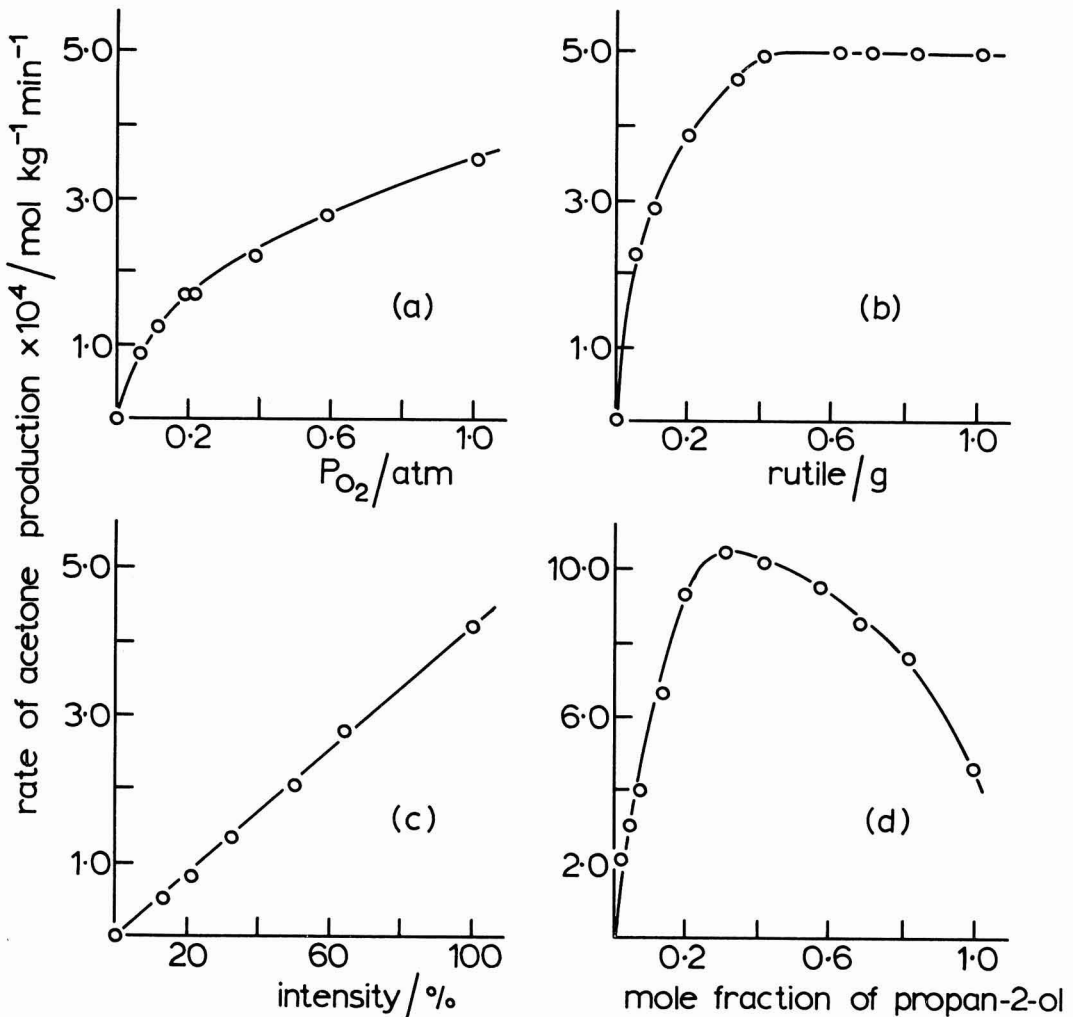


Fig. 2. The effects of oxygen pressure (a), weight of oxide (b), radiation intensity (c), and water concentration (d), on the rate of acetone production from pure rutile

Figure 3. Unlike pure rutile, the majority of these plots show an increase in reaction rate over the first  $\sim 100$  min, but the subsequent linear portions were used to calculate the rates given in Table 1. The data show that a well defined sequence of photoactivity for the pigments can be determined from experiments of 300 minutes duration. The sequence shows expected features that rutile pigments coated with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  were considerably less active than uncoated anatase or rutile, and in that the activity was not directly proportional to the specific surface area. In addition, it is shown that surface treatment with organic compounds does not necessarily ensure low photoactivity.

For comparative purposes, the chalking resistance of a number of the pigments was assessed by conventional accelerated tests exposing painted panels in a Marr weathering machine. With a thermosetting acrylic medium and pigment/resin ratios of 1:1 and 0.6:1, weight losses after irradiation

for 3500 hours gave the photoactivity sequence:  $2 \gg 4 > 6 > 5 \sim 10 > 7 \sim 9$ . Similar tests of 1200 hours duration with a coconut oil alkyd/melamine formaldehyde medium gave the sequence  $2 \gg 4 \sim 5 > 6 \sim 10 > 7 \sim 9$ . Clearly, there is a considerable measure of agreement between these two sequences and that determined from the rate of acetone production in experiments of markedly shorter duration. On the basis of this correlation it is suggested that the photocatalytic oxidation of propan-2-ol could form the basis of a rapid method of assessing the photoactivity of both coated and uncoated  $\text{TiO}_2$  pigments.

Buss *et al*<sup>16</sup> recently reported that the photo-oxidation of liquid methanol, ethanol and butan-1-ol occurs at the expense of lattice oxygen in anatase  $\text{TiO}_2$  when gaseous oxygen was excluded, and that there was a marginal increase in activity with an increase in the molecular weight of the alcohol. This prompted the authors to investigate the possibility that other alcohols might provide an alternative rapid test of pigment

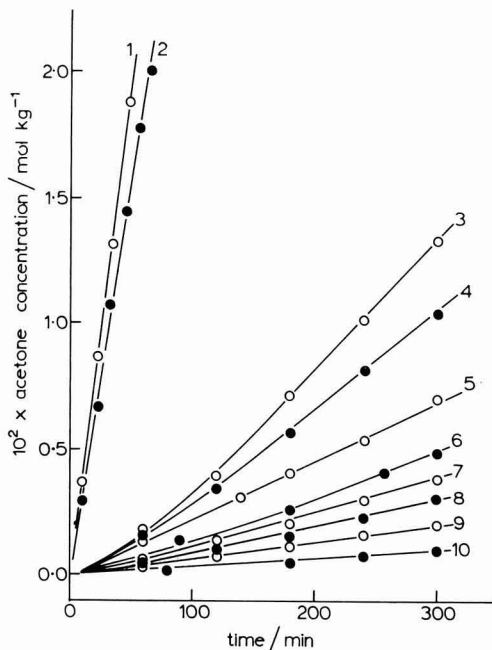


Fig. 3. Acetone production from pure rutile and nine commercial pigments (details given in Table 1)

photoactivity. Measurements<sup>17</sup> showed that the photocatalytic oxidation of ethanol to acetaldehyde and ethyl

acetate, propan-2-ol to acetone, and butan-2-ol to butanone occurred at closely similar rates on pure rutile at 293K. The relative ease in obtaining pure starting material, coupled with a single reaction product, makes propan-2-ol the preferred reactant.

[Received 6 October 1977]

## References

- Brand, B. G., Nowacki, L. J., Mirick, W., and Muller, E. R., *J. Paint Technol.*, 1968, **40**, 396.
- Sullivan, W. F., *Progr. Org. Coatings*, 1972, **1**, 157.
- Goodeve, C. F., and Kitchener, J. A., *Trans. Faraday Soc.*, 1938, **34**, 570.
- Weyl, W. A., and Forland, T., *Ind. Eng. Chem.*, 1950, **42**, 257.
- Mushii, R. Ya., and Pamfilov, A. V., *Ukrainskii Khim. Zhur.*, 1958, **24**, 462.
- Wilksa, S., *JOCCA*, 1967, **50**, 911.
- Jacobsen, A. E., *Ind. Eng. Chem.*, 1949, **41**, 523.
- Poisson, R., Petit, J., and Fischer, J., *Peintures, Pigments, Vernis*, 1964, **40**, 277.
- Ilenko, V. S., Uvarov, A. V., and Milko, V. I., *Zavodskaya Laboratoriya*, 1973, **39**, 1089.
- Irick, G., *J. Appl. Pol. Sci.*, 1972, **16**, 2387.
- Cundall, R. B., Rudham, R., and Salim, M. S., *J. C. S. Faraday I.*, 1976, **72**, 1642.
- Richardson, P. C., Rudham, R., Twist, W., and Wagstaff, K. P., *Trans. Faraday Soc.*, 1970, **66**, 1773.
- Bickley, R. I., and Stene, F. S., *J. Catalysis*, 1973, **31**, 389.
- Boonstra, A. H., and Mutsaers, C. A. H. A., *J. Phys. Chem.*, 1975, **79**, 1694.
- Hird, M. J., *J. Coatings Tech.*, 1976, **48**, 75.
- Buss, A. D., Malati, M. A., and Atkinson, R., *JOCCA*, 1976, **59**, 369.
- Rudham, R., and Ward, S., *Unpublished observations*.

# The role of the Diels-Alder reaction in the curing of drying-oil alkyd-melamine systems

By K. Holmberg

Berol Kemi AB, Division SOAB, Box 55, 431 21 Mölndal, Sweden

## Summary

Alkyd resins based on drying oils often give harder films than those based on non-drying oils when cured with melamine resins at the same alkyd/melamine ratio under acidic conditions. This difference

can be explained by a contribution to the crosslinking by a Diels-Alder reaction between conjugated double bonds in the fatty acid chains and an imino group derived from the melamine resin.

## Keywords

*Types and classes of coatings and allied products*

catalysed coating  
stoving finish

*Raw materials  
binders (resins, etc.)*

melamine alkyd resin

*Processes and methods primarily associated with  
drying or curing of coatings*

Diels-Alder reaction

*Miscellaneous terms*

Diels-Alder reaction

## Le rôle de la réaction de Diels-Alder dans le durcissement des mélanges de résines alkydes à base d'huiles siccatives et des résines mélaminées

### Résumé

Durcies par les résines mélaminées au même rapport alkyde/mélamine, et sous les conditions acides, les résines alkydes à base d'huiles siccatives rendent souvent les films plus durs que celles à base d'huiles non siccatives. On peut expliquer cette différence en

proposant que le niveau de réticulation est augmenté par une réaction de Diels-Alder entre les liaisons doubles conjuguées dans les chaînes des acides gras et un groupement imino dérivé de la résine mélamine.

## Die Rolle der Diels-Alder Reaktion bei der Härtung von trocknendes Öl enthaltenden Alkyd-Melaminsystemen

### Zusammenfassung

Wenn auf trocknenden Ölen basierende Alkydharze mit Melaminharzen zusammen gehärtet werden, sind ihre Filme oft härter, als auf nichttrocknenden Ölen basierende mit dem selben Alkyd/Melamin-Verhältnis unter sauren Bedingungen. Dieser Unterschied

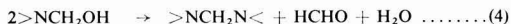
kann durch einen Beitrag zur Vernetzung durch eine Diels-Alder Reaktion zwischen konjugierten Doppelbindungen in den Fettsäureketten und einer vom Melaminharz herrührenden Imino-Gruppe erklärt werden.

## Introduction

*Refs. 1, 2*

Melamine resins are of importance as crosslinking agents for polymers, such as alkyds, polyesters and acrylic resins. The crosslinking is accomplished by heating, by the influence of an acid catalyst or by a combination of each<sup>1,2</sup>.

amino resin may take place, particularly when the concentrations of >NH and >NCH<sub>2</sub>OH are high (reactions 3 and 4, respectively)<sup>3-8</sup>.



Consequently, the hydroxyl groups in the alkyd are mainly responsible for the crosslinking with melamine resin. (The catalytic effect of the carboxyl groups can probably be neglected when strong acids, such as p-toluenesulfonic acid, are used as external catalysts.)

However, when drying-oil alkyds are used, other curing mechanisms must also be operative, since at the same alkyd/melamine ratio these alkyds often give harder films than alkyds based on non-drying oils. This has been explained by an additional crosslinking, due to either oxidative polymerisation involving olefinic groups or etherification of hydroxyl groups formed on fatty acid residues by oxidation. However, these reactions are normally sluggish, and it

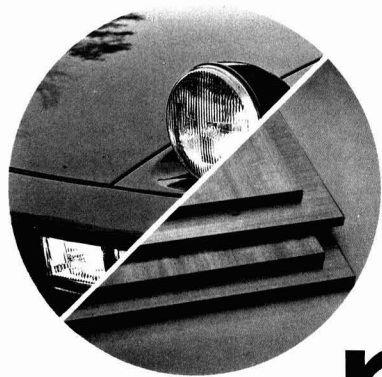
## Curing reactions

*Refs. 3-8*

In recent years, owing to the high costs of energy, more and more attention has been directed towards low temperature acid cured systems. A great deal of work has been carried out to investigate the crosslinking reactions occurring in these systems. It seems to be generally accepted that the main reactions taking place under acidic conditions between a melamine resin and a hydroxyl/carboxyl containing polymer, such as an alkyd, are condensations between alkoxyethyl and hydroxymethyl groups of the melamine and the hydroxyl groups of the other component (reactions 1 and 2, respectively). In addition, a certain degree of self-crosslinking of the

Henkel

Henkel



Henkel  
makes  
good  
paints  
even better

# PERENOL® E1

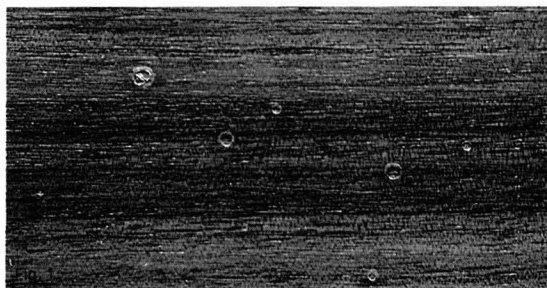
Silicone-free air-release agent for solventless and solvent-based coatings.

Both in the manufacture and the application of paints, one of the main difficulties is to prevent the formation of bubbles or to eliminate any bubbles emerging from the substrates which are being coated. This applies not only to aqueous systems but in particular also to solventless and solvent-based coatings.

In addition non-gelatinizing and bi-functional special plasticizers for furniture lacquers are in our product range

EDENOL BS 20 N; MS 20 N; IBS; LFW 100; LFW 101, 104

To obtain maximum performance from air-release agents, a proper balance between the paint viscosity and the drying time is an important pre-condition. With highly viscous systems, their performance may be supported by the addition of a small portion of a high-boiling solvent, whenever this is possible. In clear varnishes, the amount of PERENOL E 1 required lies between 0,05-1,0%, calculated on the finished paint. As the defoaming action is normally intensified in the presence of pigments, a dosage of 0,05-0,2% calculated on the finished paint is sufficient in most cases. In pigmented, acid-curing lacquers, a combination of PERENOL E 1 and our flow-modifier PERENOL F 3 (amount to be added: 0,1-0,2% on total system) has proved useful with regard to both anti-bubbling effect and flow properties.

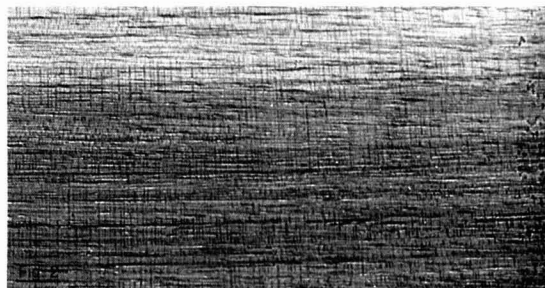


## Nitrocellulose – Curtain Coating Lacquer

- 235 pbw Nitrocellulose E 510 (Wolff, Walsrode, Germany) solution of 40% nitrocellulose, 40% butyl-acetate and 20% butanol
- 180 pbw Alkydal® E41 (Bayer, Germany) groundnut-oil type, 40% oil content, 70% in xylene
- 15 pbw Di-butyl phthalate
- 15 pbw EDENOL® BS 20 N
- 185 pbw Toluene
- 120 pbw Isopropanol
- 110 pbw Spirit 110/140
- 100 pbw Butyl acetate
- 40 pbw Silicone Oil A, 1% in Toluene (Bayer, Germany)

1000

solid substance 25%, Viscosity 32-36 DIN 4 sec.



## Paints in contact with foodstuffs

PERENOL E 1 meets the requirements laid down in the 47th Information of the German Federal Health Board, XL-paints and coatings for food containers and packings.

However, it is decisive for the user to observe Section B/II which defines the requirements the ready-to-use coatings must meet. It stipulates that "by taking into consideration their composition, the coatings must be dried in a manner which prevents any volatile constituents, particularly any solvents, from passing into the foodstuffs or onto their surfaces".

Fig. 1 Nitro-cellulose curtain coating, R-LH 27-19, without PERENOL E1

Fig. 2 Nitro-cellulose curtain coating, R-LH 27-19, 0,5% PERENOL E1



# PERENOL® S 4

Slip-agent for solvent-containing and solvent-free finishes. Improves the scratch and soiling resistance and flow properties. Suitable for paints based on air-drying alkyd resins, alkyd/melamine resin combinations, air-drying, self and other cross-linking polyacrylic resins, polyurethanes, nitrocellulose, oilfree polyesters. Dosage 0,1-0,5% calculated on the finished paint.

**Fields of application:** PERENOL S 4 is suitable for use in coatings based on  
 air-drying alkyd resins  
 alkyd melamine combinations  
 acrylic resins (self-crosslinking and 2-component systems)  
 polyurethanes  
 nitrocellulose lacquers  
 acid-curing melamine and urea resins  
 oilfree polyesters



**Guide Formula – No. R-LH-67-7**  
 2-Component Acrylic Resin Paint, Yellow  
 338,4 pbw Hydroxyl group containing acrylic resin,  
 60% sol. in xylene/butylacetate  
 (e.g. MACRYNAL® SM 540)<sup>1)</sup>  
 145,8 pbw Hydroxyl group containing acrylic resin,  
 50% sol. in xylene/butylacetate  
 (e.g. MACRYNAL® SM 548)<sup>1)</sup>  
 155,1 pbw Titanium dioxide Rutile (e.g. TiO<sub>2</sub>RKB 3)<sup>3)</sup>  
 155,1 pbw Chrome yellow (e.g. Chrome Yellow 630 L)<sup>2)</sup>  
 29,1 pbw Ethylglycol acetate  
 101,0 pbw Xylene  
 8,3 pbw Butyl acetate  
 67,3 pbw Aliphatic Isocyanate, 75% sol. in xylene/  
 ethylglycol acetate  
 (e.g. DESMODUR®N 75)

0,5% PERENOL S 4 is added calculated on the undiluted paint. Solid content approx. 64%, Pigment volume concentration approx. 16%, Stove drying 20-30 min/100-130°C

Please forward – free-of-charge and without obligation – the following samples and technical leaflets:

- PERENOL® E 1
- PERENOL® S 4
- PERENOL® S 5
- PERENOL® F 3
- EDENOL®-TYPE PLASTICIZERS

Name .....

Position .....

Company .....

P. O. Box/Street .....

Town/City .....

Country .....

Please forward – free-of-charge and without obligation – the following samples and technical leaflets:

- PERENOL® E 1
- PERENOL® S 4
- PERENOL® S 5
- PERENOL® F 3
- EDENOL®-TYPE PLASTICIZERS

Name .....

Position .....

Company .....

P. O. Box/Street .....

Town/City .....

Country .....

# PERENOL® S5

Slip-agent for aqueous varnishes (air and stove drying, water-reducible paints). PERENOL S 5 improves the scratch and soiling resistance and flow of the top-coat. No side-effects have been observed. The dosage lies between 0,1-0,5% calculated on the finished paint.

The technical properties of PERENOL S 5 are the same as those of PERENOL S 4. However, on account of the water-tolerance of this products' solvent it is particularly suitable for use in water-reducible air-drying paints and stoving enamels.

## Guide Formula – No. LH-77-20

Water-reducible stoving enamel, white

147 pbw Acrylic resin, neutralizable, amine resin wetting 70% sol. in alcohols and glycol-ethers (e.g. RESYDROL® VWY 23)<sup>1)</sup>

178 pbw Titandioxide (e.g. KRONOS RN 59)<sup>2)</sup>

147 pbw Acrylic resin, neutralizable, amine resin wetting, 70% sol. in alcohols and glycol-ethers (e.g. RESIDROL® VWY 23)<sup>1)</sup>

88 pbw Hexamethoxymethyl melamine resin, non-plasticized, 100% (e.g. MAPRENAL® MF 900)<sup>1)</sup>

20 pbw Dimethylethanol amine

80 pbw Butyl glycol

80 pbw n-Butanol

40 pbw Ethyl glycol

20 pbw Glycolic acid butyl ester

200 pbw Deionized water

1000

## Manufacturers – Guide Formula No. R-LH-67-7

<sup>1)</sup> Casella Farbwerke AG, D 6000 Frankfurt am Main, W. Germany

<sup>2)</sup> BASF, Bereich Stiegl-Farben, D 7000 Stuttgart, W. Germany

<sup>3)</sup> Farbenfabriken Bayer, D 5090 Leverkusen, W. Germany

## Manufacturers – Guide Formula No. LH-77-20

<sup>1)</sup> Farbwerke Hoechst AG, D 6230 Frankfurt am Main, W. Germany

<sup>2)</sup> Titangesellschaft AG, D 5090 Leverkusen, W. Germany

Henkel KGaA  
Organic Products Division  
Dehydtag KLF-T  
P.O.Box 1100  
D-4000 Düsseldorf 1 · Germany

Henkel KGaA  
Organische Produkte  
Dehydtag KLF-T  
Werbung  
Postfach 1100

D-4000 Düsseldorf 1

Germany

Henkel KGaA  
Organische Produkte  
Dehydtag KLF-T  
Werbung  
Postfach 1100

D-4000 Düsseldorf 1

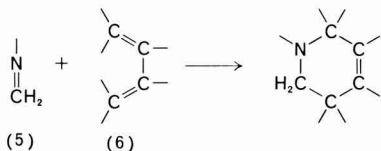
Germany

seems very unlikely that they would be able to give any significant contribution to the initial cure of the system, especially as autoxidation catalysts are not usually present. On ageing, however, the influence of the olefinic groups becomes evident, giving rise to less durable systems as a result of oxidative degradation.

### The role of the Diels-Alder reaction

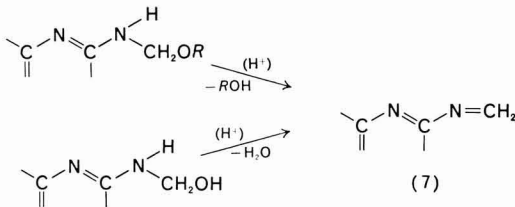
Refs. 9-17

A reaction which is probably of greater importance in explaining the effect of drying oil in the alkyd is a Diels-Alder reaction between an imino group of the melamine resin (5) and conjugated double bonds originated from the oil (6).



### The dienophile

Formation of imino groups could readily occur by an acid catalysed elimination of alcohol and water from melamine resins containing the groups  $\text{NHCH}_2\text{OR}$  and/or  $\text{NHCH}_2\text{OH}$ . The reactions are analogous to the well-known  $\beta$ -elimination leading to olefinic bonds<sup>9</sup>.



The formation of the imine (7) from melamine resins has previously been suggested by Berge *et al.*<sup>10</sup>. The reaction is, of course, a characteristic of resins containing secondary amines.

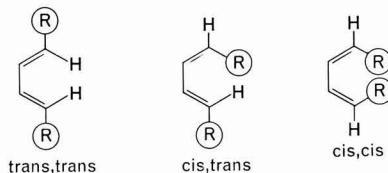
Imino bonds are generally known to function as dienophiles in Diels-Alder reactions<sup>11</sup>. Imines, such as (7), which contain an electron-attracting substituent would be expected to be especially reactive towards most dienes owing to the lowering of the energy of the lowest unoccupied orbital<sup>12</sup>. This has, in fact, been demonstrated in at least one instance<sup>13</sup>.

### The diene

Conjugated double bonds are present to a certain degree in most drying oils and fatty acids. Dehydrated castor oil (DCO), which is frequently employed in alkyds used for curing with melamine resins, contains 25-30 per cent conjugation. In addition, isolated olefinic bonds present in linoleic and linolenic acid may isomerise to form conjugated systems under acidic conditions.

Conjugated systems in fatty acid residues are known to be reactive dienes in Diels-Alder reactions, if the olefinic groups are in a cisoid-conformation<sup>14</sup>.

*Trans, trans* substituted dienes can easily satisfy this condition and are consequently active towards dienophiles<sup>15,16</sup>. In *cis, trans* and especially in *cis, cis* substituted dienes, on the other hand, the formation of the cisoid-conformation is sterically hindered through non-bonded interaction, as is illustrated below<sup>17</sup>.



The amount of *trans, trans* unsaturated systems is small in most naturally occurring oils and fatty acids. However, *cis* → *trans* isomerisation is a well-known phenomenon in the chemistry of fatty acids (elaidinisation), and it may take place both in the preparation of the alkyd and during the acid catalysed curing process. Most alkyds based on drying oils, therefore, contain a certain amount of conjugated olefinic groups capable of acting as dienes in Diels-Alder reactions.

### General considerations

Refs. 18-21

The contribution by the above-mentioned Diels-Alder reaction to the curing of drying-oil alkyd-melamine systems does not seem to have been suggested previously. The Diels-Alder reaction as such, however, is known to play an important role in the curing process of other resin systems. Oils based on conjugated acids, such as eleostearic acid, may act both as diene and dienophile, a fact which is probably one of the reasons for the good drying properties of these systems<sup>18</sup>. Rosin functions as a good dienophile in reactions with phenolic resins<sup>19</sup>, but it may also participate as diene in Diels-Alder reactions, due to isomerisation of the 1,3-diene in abietic acid to a conjugated diolefin<sup>20</sup>. Phenolic resins with free *o*-hydroxymethyl groups may undergo dehydration to give *o*-quinone methide structures which readily act as dienes towards resins containing  $\pi$ -bonds<sup>21</sup>.

### Conclusions

The Diels-Alder reaction seems to be involved in the acid-catalysed curing of drying-oil alkyd-melamine systems.

The contributory effect of the Diels-Alder reaction on the final film properties of such systems is small in comparison to other crosslinking reactions. However, the effect is still quite significant and may be of importance in borderline cases where marginal differences in curing speed and film hardness are to be taken into account.

The influence of the Diels-Alder reaction is dependent upon the type of alkyd and melamine in use. Prerequisites for the reaction to occur are the presence of conjugated double bonds in the alkyd resins and NH-groups in the melamine resin.

### Acknowledgment

The author greatly appreciates helpful discussions with Mr H. Goyaerts.

[Received 17 January 1978]

**References**

1. Solomon, D. H., "The chemistry of organic film formers", Wiley, New York 1967, 222.
2. Rutter, L. A., *Paint Manuf.*, 1974, April 8.
3. Blank, W. J., and Hensley, W. L., *J. Paint Techn.*, 1974, **46**, 46.
4. Seidler, R., and Stolzenbach, H. G., *Farbe und Lack*, 1975, **81**, 281.
5. Daehre, K.-H., *Plaste und Kautschuk*, 1976, **23**, 923.
6. Wohnsiedler, H. P., *ACS Div. Org. Coatings & Plastics Chem.*, 1960, **20/2**, 53.
7. Dörffel, J., and Biethan, U., *Farbe und Lack*, 1976, **82**, 1017.
8. Saxon, R., and Lestienne, F. C., *J. Appl. Pol. Science*, 1964, **8**, 475.
9. Carruthers, W., "Some modern methods of organic synthesis", Cambridge Univ. Press, London, 1971, 71.
10. Berge, A., Kvaeven, B, and Ugelstad, J., *Europ. Pol. J.*, 1970, **6**, 981.
11. Gilchrist, T. L., and Storr, R. C., "Organic reactions and orbital symmetry", Cambridge Univ. Press, London, 1972, 92.
12. Fukui, K., in "Molecular orbitals in chemistry, physics and biology", Löwdin, P. O., and Pullman, B. (Eds.), Academic Press, New York, 1964, 513.
13. *Ref. 9*, 123.
14. *Ref. 9*, 131.
15. Bickford, W. G., Hoffman, J. S., Heinzelman, D. C., and Fore, S. P., *J. Org. Chem.*, 1957, **22**, 1080.
16. Teeter, H. M., O'Donnell, J. L., Schneider, W. J., Gast, L. E., and Danzig, M. J., *J. Org. Chem.*, 1957, **22**, 512.
17. Paschke, R. F., and Wheeler, D. H., *J. Am. Oil Chemists' Soc.*, 1955, **32**, 469.
18. Wheeler, D. H., *Offic. Dig. Federation Soc. Paint Technol.*, 1951, **23**, 661.
19. Hultzsck, K., "Chemie der Phenolharze", Springer-Verlag, Berlin, 1950, 78, 156.
20. *Ref. 1*, 73.
21. Sprengling, G. R., *J. Am. Chem. Soc.*, 1952, **74**, 2937.

# The mechanism of the acid catalysed curing of alkyd-melamine resin systems

By K. Holmberg

Berol Kemi AB, Division SOAB, Box 55, 431 21 Mölndal, Sweden

## Summary

The co-condensation of alkyds and melamine resins, as well as the self-condensation of melamine resins, is suggested to proceed by a bimolecular displacement reaction of the  $S_N2$  type. This implies that the rate of cure is dependent upon the nature of the groups

being removed from the melamine resin and the nucleophiles of the alkyd, and that the rate is proportional to the concentration of the reacting groups in both resin components.

## Keywords

*Types and classes of coating and allied products*

catalysed coating  
stoving finish

*Raw materials*

binders (resins, etc.)

melamine alkyd resin

*Processes and methods primarily associated with drying or curing of coatings*

catalytic curing

## Le mécanisme du cuisson des systèmes de résines alkyde-mélatamines par les catalysateurs acides

### Résumé

On suggère que la co-condensation des résines alkydes et des résines mélaminées, ainsi que l'auto-condensation de celles-ci, se produisent selon une réaction de déplacement bi-moléculaire du type  $S_N2$ . Cela implique que la vitesse de cuisson se dépend de la

nature des groupements qui sont éliminés de la résine mélamine et des nucléophiles de la résine alkyde, et d'ailleurs que la vitesse est proportionnelle à la concentration des groupements en réaction dans les deux constituants résineux.

## Der Mechanismus säurekatalysierter Alkyd-Melaminharzsysteme

### Zusammenfassung

Es wird vorgeschlagen, dass sowohl die Kokondensation von Alkyden und Melaminharzen, als auch die Selbstkondensation von Melaminharzen mittels einer bimolekularen Verschiebungsreaktion vom  $S_N2$  Typ erfolgt. Dies bedeutet, dass die Härtungsge-

schwindigkeit von den vom Melaminharz entfernten Gruppen, sowie den Nucleophilen des Alkydes abhängig ist, und dass die Geschwindigkeit proportional zur Konzentration der reagierenden Gruppen in beiden Harzkomponenten ist.

## Introduction

*Refs. 1-10*

The chemistry of the curing process of alkyd-melamine resin systems has been under investigation for about two decades. The first detailed study on the subject appears to be Wohnsiedler's work<sup>1</sup>, published in 1960, in which it was shown that the alkyd resin not only exerts a plasticising function, but is also directly involved in the crosslinking of the system. Wohnsiedler considered reactions between hydroxyl groups in the alkyd and alkoxymethyl and hydroxymethyl groups in the melamine resin as the most important in co-condensation, however, several other possibilities were also indicated. The self-condensation of melamine resins leads to the formation of methylene linkages between the aminotriazine structures with a simultaneous loss of alcohol and formaldehyde, as was shown by IR-spectroscopy.

polymers has been supported by other authors<sup>2,3</sup>, however, dissentient views have been expressed also<sup>4</sup>. One study not only dealt with the condensation reactions taking place in the resin mixture, but also considered possible hydrolytic reactions occurring prior to and parallel with the formation of the network<sup>5</sup>.

The self-curing of melamine resins has been found to be favoured by high concentrations of  $>NH$  and  $>NCH_2OH$  groups, and in resins rich in these groups the self-condensation seems to be the predominant process, even in the presence of hydroxyl-rich alkyds<sup>3,6,7</sup>. The self-condensation is believed to proceed either by reaction of two hydroxymethyl groups with elimination of formaldehyde and water, or by condensation of one hydroxymethyl and one secondary amino group, in both cases leading to the methylene bridge as suggested by Wohnsiedler.

Wohnsiedler's work has been the basis for more thorough investigations of the curing process. Due to its structural simplicity, hexakis (methoxymethyl)-melamine (HMMM) has been the model melamine compound most widely used in these experiments.

However, unless the pH is kept low the alkoxymethyl group is not very reactive towards hydroxyl groups. The curing of melamine resins with hydroxyl-containing polymers is, therefore, normally accomplished in the presence of an acid catalyst. Free carboxyl groups in alkyds have been shown to exert a considerable action in this respect<sup>8</sup>, but in order to increase the reaction rate still further, external catalysts, such as *p*-toluene-sulfonic acid, are usually employed<sup>9,10</sup>. It has

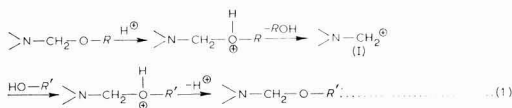
Wohnsiedler's view of transesterification being the predominant curing reaction with hydroxyl/carboxyl containing

been shown that the acid not only catalyses the desired co-condensation, but also enhances the rate of reactions leading to self-condensation of the melamine resin.

### The role of the acid catalyst

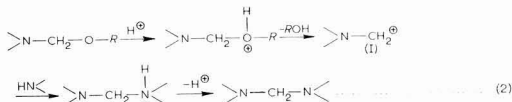
Refs. 11-18

The role played by the acid catalyst has been the topic of several investigations. A multi-stage mechanism proceeding via a primary carbonium ion (I) has been suggested for the decomposition of melamine resins<sup>11</sup>, as well as for the co-condensation of melamine resins with alkyds and polyacrylates<sup>12,13</sup>. The reaction between an alkyd and a melamine resin is shown below:



(where  $R$  may be either hydrogen or an alkyl group and  $R'$  is the alkyd residue).

An analogous mechanism has been proposed for the self-condensation of melamine resins<sup>14,15</sup>:



Consequently, the main reactions taking place in the co-condensation process, as well as in self-condensation, have been proposed to proceed by a conventional  $S_N1$  type mechanism. This would imply that the rate expression for the reaction (1) between alkyds and melamine resins is of first order, *i.e.*, at a constant temperature the rate of reaction would be dependent only on the concentration of the amino resin and be independent of the concentration of the alkyd component:

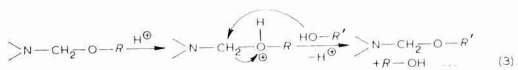
$$\text{that is, } \text{rate} = k \cdot [\text{>N-CH}_2\text{-O-R}]$$

However, the reaction mechanisms (1) and (2) above seem rather unlikely for several reasons. The only organic compounds that undergo reaction by an  $S_N1$  path are those capable of forming relatively stable carbonium ions. Unless extreme electronic stabilisation is at hand,  $S_N1$  reactions do not take place on primary carbon atoms. In this particular case, the postulated intermediate (I) is strongly destabilised due to the electron-withdrawing effect exerted by both the adjacent nitrogen atom and its electron-attracting substituents. Consequently, the formation of the carbonium ion (I) as a reaction intermediate seems improbable for electronic reasons.

Furthermore, if the displacement reaction is of first order, the rate of cure would be independent of the type and concentration of nucleophilic groups in the alkyd. This is not consistent with the finding that an increase in the hydroxyl value of the alkyd leads to faster cure and to harder films<sup>16</sup>, and that primary hydroxyl groups are more reactive than secondary ones<sup>17</sup>. Indeed, it has been shown that the two resin components are of equal importance in the curing process<sup>18</sup>, a fact which implies that they are both involved in the rate-determining step of the co-condensation reaction.

Whereas neither theoretical considerations nor experimental results are in harmony with an  $S_N1$  reaction, they are fully

consistent with a bimolecular nucleophilic substitution reaction of the  $S_N2$  type. The reaction between hydroxyl groups in the alkyd and alkoxyethyl or hydroxymethyl groups in the melamine resin could then be depicted as follows:



(where  $R$  may be hydrogen or an alkyd group and  $R'$  is the alkyd residue).

The rate-determining step is a nucleophilic attack by the alkyd hydroxyl group on the primary carbon atom with a simultaneous loss of alcohol or water. The rate of reaction is dependent on the concentration and the reactivity of the nucleophile (alkyd-OH), as well as on the nature of the group being removed (alcohol or water from the melamine resin) and may be expressed as:

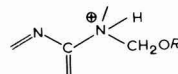
$$\text{rate} = k \cdot [\text{>N-CH}_2\text{-O-R}] \cdot [\text{HO-R}']$$

Similarly, an  $S_N2$ -type of displacement reaction offers a probable mechanistic explanation for the reaction between hydroxymethyl and secondary amino groups of melamine resins resulting in self-condensation. The attacking nucleophile in this reaction is the secondary amine and the rate of reaction is dependent upon the concentrations of both groups involved.

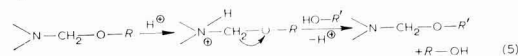


Since nucleophilic displacements on primary carbon atoms almost invariably proceed by the  $S_N2$  reaction, the mechanisms of reactions (3) and (4) seem logical. The electron-attracting effect by the adjacent nitrogen atom and by its substituents will only increase the  $S_N2$  reactivity further, due to the increased electrophilic character of the primary carbon.

Under acidic conditions a certain degree of protonation of the amino nitrogens external to the ring of the melamine resin is likely to occur.



The N-protonation would effectively prevent the formation of the carbonium ion (I) and thus render the  $S_N1$  reaction impossible. However, a bimolecular displacement of the  $S_N2$  type is still feasible:



### Conclusions

Mechanisms according to the reactions (3) and (4) for the co-condensation and the self-condensation of the alkyd-melamine resin system seem to explain experimental facts and are also consistent with theoretical considerations. Since the rate-determining steps of the reactions are bimolecular, the curing process is affected by variations of each of the resin components involved.

The question of whether the acid-catalysed reaction between alkyds and melamine resins proceeds by  $S_N1$ - or

**OIL & COLOUR  
CHEMISTS' ASSOCIATION**

Newcastle Section Symposium



**ULTRAVIOLET POLYMERISATION  
AND THE  
SURFACE COATING  
INDUSTRIES**

# UV2 UV2

The eleven papers in this volume were originally published in the *Journal* earlier in 1978. They are based on lectures given at the Second International Symposium of the Newcastle Section of the Association held at Durham University on 14 and 15 September 1977. Titles and authors are listed below:

Exciplex interactions in photoinitiation of polymerisation by fluorenone amine systems *by A. Ledwith, J. A. Bosley and M. D. Purbrick*

Recent developments in photoinitiators *by G. Berner, R. Kirchmayr and G. Rist*

Present status of ultraviolet curable coatings technology in the United States *by J. Pelgrims*

The design and construction of ultraviolet lamp systems for the curing of coatings and inks *by R. E. Knight*

New developments in ultraviolet curable coatings technology *by C. B. Rybny and J. A. Vona*

Cure behaviour of photopolymer coatings *by R. Holman and H. Rubin*

Photoinitiator problems in clear coatings *by M. De Poortere, A. Ducarme, P. Dufour and Y. Merck*

The UV curing of acrylate materials with high intensity flash *by R. Phillips*

Parameters in UV curable materials which influence cure speed *by A. van Neerbos*

The use of differential scanning calorimetry in photocuring studies *by A. C. Evans, C. Armstrong and R. J. Tolman*

The UV curing behaviour of some photoinitiators and photo-activators *by M. J. Davis, J. Doherty, A. A. Godfrey, P. N. Green, J. R. A. Young and M. A. Parrish*

**To obtain this book, complete the order form below and send with the necessary remittance to the Association's offices. Price: £7.50 (US \$15) each.**

**ORDER FORM  
(PREPAYMENT ONLY)**

To: The Director and Secretary,  
Oil & Colour Chemists' Association,  
Priory House,  
967 Harrow Road,  
Wembley, Middx.,  
HA0 2SF  
England.

Date .....

Please send me ..... copy(ies) of Ultraviolet Polymerisation 2 at £7.50 (US \$15) each.

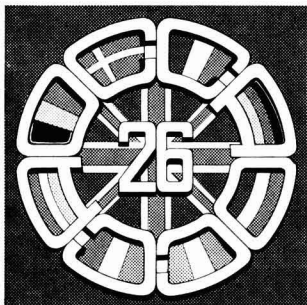
I enclose remittance of £ (US \$) ..... to cover the cost. (Prepayment only)

NAME .....

ADDRESS TO WHICH THE BOOKS SHOULD BE SENT:  
.....  
.....  
.....

# "The OCCA"

The annual technical exhibition of the Oil and Colour Chemists' Association (known to many simply as "The OCCA") has become the world's most important event for all those connected with the paint, printing ink, polymer, adhesive, colour and allied manufacturing industries. The OCCA exhibition is held every year in London, England. The symbols for the 1974-79 exhibitions were specially designed by Robert Hamblin, Director and Secretary of the Association, to emphasise the very wide coverage which all the Association's activities attract:



The motif for OCCA-26 used the flags of the enlarged EEC converging on the British flag to symbolise the welcome extended to visitors from overseas to the Exhibitions for more than 25 years. (1974)

## The INTERNATIONAL Focal Point for the Surface Coatings Industries



The motif for OCCA-31 emphasises the unique aspect of the OCCA Exhibitions, which annually provide an international focal point for the surface coatings industries.



The 1974 theme continued at OCCA-27 by showing the world-wide interest aroused by the Association's annual Exhibitions in London which attract visitors from all parts of the globe.

The OCCA Exhibitions provide a unique annual focal point for the surface coatings industries, and bring together technical personnel to meet in an informal atmosphere allowing a free interchange of ideas and the rapid dissemination of knowledge of new products and new developments of existing products.

In recent years, visitors to the OCCA Exhibitions have regularly come from over fifty overseas countries and at the 1978 Exhibition, admissions by season ticket of over 10,000 were recorded at the turnstiles in the hall.

The Exhibition provides an ideal opportunity for organisations to display and discuss their products and services to a wide spectrum of visitors from all over the world.

Organisations wishing to receive further details should contact the Director & Secretary, Mr R. H. Hamblin, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, England (Tel: 01-908 1086, Telex: 922670 OCCA G).



The motif for OCCA-30 used the symbol of a moving indicator on a calendar to emphasise the importance of the continuous dialogue year by year between suppliers and manufacturers.



The motif for OCCA-28 emphasised that the target for 1976 was London where all the Exhibitions have been held, and continued the theme of its international aspect.



In 1977 the motif for OCCA-29 used inward pointing arrows to show the many places from which people came to the Exhibition, and these arrows formed outward pointing arrows to show the subsequent spreading of knowledge.



$S_N2$ -mechanism is not purely of academic interest. As the rate of cure is dependent on the nature of the attacking nucleophile, groups with stronger nucleophilic action than hydroxyl groups may be incorporated into the alkyd in order to increase the rate of reaction with amino resin. Such experiments have, in fact, recently been reported by Massy *et al*<sup>19</sup>, who incorporated thiol groups into alkyds by esterification of the hydroxyl groups with mercapto-acids. The thiol-containing alkyds were found to be considerably more reactive towards amino resins than the corresponding non-modified alkyds. Incorporation of other strong nucleophiles, such as amino groups, into alkyds could be expected to lead to similar results.

### Acknowledgment

The author wishes to thank Mr H. Goyaerts for helpful suggestions.

[Received 17 February 1978]

### References

1. Wohnsiedler, H. P., *ACS Div. Org. Coatings & Plastics Chem.*, 1960, **20/2**, 53.
2. Dörrfel, J., and Biethan, U., *Farbe und Lack*, 1976, **82**, 1017.
3. Seidler, R., and Graetz, H. J., *VI FATIPEC-kongress*, 1962, 282.
4. Stromberg, S. E., *ACS Div. Org. Coatings & Plastics Chem.*, 1969, **29/2**, 321.
5. Hornung, K.-H., and Biethan, U., *Farbe und Lack*, 1976, **76**, 461.
6. v. Zuylen, J., *J.O.C.C.A.*, 1969, **52**, 861.
7. Seidler, R., and Stolzenbach, H. G., *Farbe und Lack*, 1975, **81**, 281.
8. Augustsson, L., *Färg och Lack*, 1965, **11**, 188.
9. Blank, W. J., and Hensley, W. L., *J. Paint Technol.*, 1974, **46**, 46.
10. Koral, J. N., and Petropoulos, J. C., *J. Paint Technol.*, 1966, **38**, 600.
11. Berge, A., Kvaeven, B., and Ugelstad, J., *Europe. Pol. J.*, 1970, **6**, 981.
12. Daehre, K.-H., *Plaste und Kautschuk*, 1976, **23**, 923.
13. Saxon, R., and Daniel, jr, J. H., *J. Appl. Pol. Science*, 1964, **8**, 325.
14. Berge, A., in *Proceedings of the 3rd Intern. Conf. in Org. Coating Science and Technology*, Athens, 1977, p. 31.
15. Saxon, R., and Lestienne, F. C., *J. Appl. Pol. Science*, 1964, **8**, 475.
16. Lorimer, J. W., *J. Paint Technol.*, 1968, **40**, 586.
17. Biethan, U., Hornung, K.-H., and Peitscher, G., *Chem.-Zeitung*, 1972, **96**, 208.
18. Bohler, A. Ø., *Färg och Lack*, 1970, **16**, 113.
19. Massy, D. J. R., Winterbøttom, K., and Moss, N. S., *J.O.C.C.A.*, 1977, **60**, 446.

---

## Next month's issue

The Honorary Editor has accepted the following papers for publication, and they are expected to appear in the October issue of the *Journal*:

Synthesis of modified phthalocyanine compounds suitable as pigments by N. A. Ghanem, A. M. Naser, M. F. Ismail and M. A. Ghafar

Recent aspects of some coloured urea/dibasic acid fusion adducts by A. M. Naser, M. M. Naoum, A. A. Salman and A. Taha

Cellulose based resins for surface coatings by M. A. Zahoor, S. Chandra and A. K. Vasishta

Ship's trials of oleoresinous antifouling paints. Part I: Formulations with high and medium toxicant contents by V. Rascio, C. A. Giudice, J. C. Benitez and M. Presta

# Correspondence

---

## Lung cancer mortality. An epidemiological survey

Sir,

Your June issue contained a note on the lecture given to the Manchester section on 13 March 1978 by myself and Mr M. Hobbs of I.C.I., entitled "Lung cancer mortality of workers in chromate pigment manufacture: An epidemiological survey". It is hoped to publish this lecture in a later issue of your *Journal*, and the results of the study have already been summarised in the *Lancet* (1978, **I**, p.384), but in the meantime it may be helpful to some readers if I amplify the note's brief remarks about the survey findings.

The survey dealt mainly with the lung cancer mortality of 646 workers at three factories who entered employment before 1968 and stayed for at least one year.

Lead chromate was the main product at Factories *A* and *B*, but zinc chromate was also made at Factory *A* until 1964 and at Factory *B* until 1976; workers had mixed exposures to both products. Lung cancer mortality has been significantly higher than normal among workers with "high" or "medium" exposure who started work at Factory *A* during 1932-1954 (8.2 deaths expected, 18 observed) and at Factory *B* during

1948-1967 (1.4 deaths expected, 7 observed). However, there have been no lung cancer deaths so far among men who started work at Factory *A* during 1955-1967; various improvements in working conditions were made there in 1955. Nor have lung cancer deaths among "low" exposure workers at either factory been higher than normal. Lead chromate has always been the only product at Factory *C*, and there has been no excess of lung cancer deaths among men there starting work from 1946-1967 (2.8 deaths expected, 2 observed).

The absence of excess mortality at Factory *C* suggests that the hazard at Factories *A* and *B* arose from the manufacture of zinc chromate pigments; hopefully the apparent cessation of risk after 1955 at Factory *A* indicates that the hazard can be controlled by "good housekeeping". The survey findings suggest that under today's stricter industrial hygiene conditions the manufacture or use of lead chromate pigments should not present a lung cancer hazard.

Yours faithfully,

JOAN M. DAVIES, PHD.

*Division of Epidemiology,  
Institute of Cancer Research,  
Sutton, Surrey SM2 5PX*

1 August 1978

---

## British Standards 5082 and 5358

### Water-thinned and solvent-thinned wood primers

Sir,

There are encouraging indications of increasing interest in and use of specifications BS 5082 and 5358 for water-thinned and solvent-thinned wood primers, together with some reported difficulties in carrying out the tests specified and interpreting results. It has been proposed to the BSI that an attempt be made to revise the specifications (in particular BS 5082) and to reconcile the two different exposure test methods, as the test panels required, particularly those for BS 5082, are proving to be difficult to obtain or to produce. A comparison of the two methods has been made and further work is in progress.

It would be helpful to BSI and the writers to hear from anyone with observations to make on these standards.

One particular aspect is that of the development of blue stains and surface mould, which have been found in com-

parative exposure tests of both types of primer to be greater on a number of samples than on the control (lead-based) primer. Such growth is detrimental to subsequent paint performance, but only BS 5358 has a requirement to restrict it. Growth was not noticed on the early examples of water-thinned primers on which the specification was based. There is thus a need to bring BS 5082 into line, and meanwhile for manufacturers to consider the incorporation of fungicides, since even if their primers meet all the requirements of BS 5082, they would be unsatisfactory if prone to excessive mould growth.

Yours faithfully,

P. Whiteley  
G. L. Holbrow\*

*Building Research Establishment,  
Garston,  
Watford WD2 7JR*

*\*Paint Research Association,  
Waldegrave Road,  
Teddington,  
Middx TW11 8LD*

4 August 1978

---

## Section Proceedings

### Auckland

#### Fire safety in the chemical industry

At the monthly meeting of the Auckland Section, held at the Auckland Leagues club on Tuesday 27 June, the Chairman, Mr R. Ness, introduced Mr M. Perkins, BSc, Fire Safety Officer of the N.Z. Fire Service, who showed a film and spoke about 'Fire safety in the chemical industry'. The film clearly

showed how solvent fumes can spread from a container across the floor, to be ignited from a source of ignition some considerable distance away, and pointed out bad practices in handling solvents and means of preventing spillage. Using examples of fires from overseas and in New Zealand, Mr Perkins described the measures which should be taken to reduce the possibility of fires. The 51 members present showed their appreciation and interest by the many questions and comments which were 'fired' at Mr Perkins.

A.M.

# Review

## XIVth FATIPEC Congress 1978

### Hungarian Chemical Society

#### Papers Pp 743. Official Yearbook Pp 122

The volume contains the proceedings of the XIV Congress of the Federation of the Associations of the Paint and Printing Ink Chemists of Continental Europe, held in Budapest, Hungary, 4-9 June, 1978.

The trend of thinking and work in the field of surface coatings during recent years is presented in 99 papers by about 200 authors from all over the world. Accordingly, the topics are immensely varied and the views often controversial, depending on the way of approach.

A systematic review of such amounts of technical information can only be compared to the task of reviewing an encyclopedia and would prove just as hopeless.

The ten plenary papers presented on behalf of the member countries and the allied Associations provide a pointer towards the main trends. They deal with the electrochemical aspects of corrosion and its prevention; with the technology of aqueous coatings, the principles and practice of pigment dispersion; the role of solvents in coatings and the controversial problem of weathering.

Electrochemistry, water-based coatings and pigment/binder interaction are frequent themes of the communications as well. Other much discussed topics are the modification and/or combination of different resin systems to suit the ever-increasing requirements of durability, as well as environmental safety. Optical characteristics of pigments are revealed by electron microscopy and the findings related to the possibilities of improvement in performance. Many of the new test methods and sophisticated instruments described seek more exact evaluation of surface coating efficiency. Others aim at better control of process parameters, automation of manufacturing and finishing technologies. Powder coating, radiation curing, application of two-component coatings, electro-

deposition were scrutinised in order to improve the efficiency of the process and the quality of the final film.

The origin of the papers is as varied as their context.

From among the 7 member countries, West Germany leads with 30 contributions, followed by Switzerland with 11, Italy 9, Hungary 7, France 6, Holland 5 and Belgium 4. There are 4 Scandinavian, 4 British and 3 USA papers. 15 papers come from other European countries: Austria, Czechoslovakia, East Germany, Poland, Rumania, and one from Japan.

This worldwide selection appears to indicate the general trend towards the scientific treatment of surface coating problems. New theories are born, others extended. Practical solutions are sought by better understanding of the physical and chemical reactions involved. Testing gets more exact, manufacture and finishing techniques more productive, safer and less prone to human error.

New materials hardly emerge. Development is directed towards the improvement of the existing ones and their adaptation to recent fields of application.

One development, however, seems to point towards a quite new coating technique. Chemiphoresis, the mechanism of depositing a polymer coating upon steel from a latex dispersion without electrical current – as yet in the stage of scientific studies – might develop in the future into an efficient coating process on the practical scale.

The lay-out of the publication is excellent, including the numerous illustrations and graphs. One editorial weakness is noticeable in the translation of the abstracts into the two other official languages. These often lack clarity.

The official Yearbook at the end of the volume contains much interesting information on the activities and members of the different Associations. It could be questioned whether this information is completely up to date, on the grounds that the titles and data on surface coatings journals appear to be at least four years old.

Dr M. L. ELLINGER

## Information Received

### New technical centre

Ameron BV Protective Coatings Division, one of Europe's leading manufacturers of protective coatings, has opened a new Fl.2.5 million technical centre adjacent to the company's headquarters in Geldermalsen, The Netherlands. The new facility has been designed to handle all quality assurance and quality control activities for Ameron products in Europe, Africa and the Middle East, providing training services for the company's customers and housing Ameron's testing and applied research and product development operations.

### Marketing agreement

Under a recent agreement, Revertex Ltd is to promote sales and distribute Scott Bader's *Polidene* vinylidene chloride copolymer emulsions to the textile industries. *Polidene* copolymers are flexible binders of low flammability, a property which is becoming increasingly important as legal restrictions

are being introduced in many markets.

### Resin capacity increased

Du Pont has announced completion of a 30 per cent capacity increase for its *Ethax* ethylene-based resins which are prime ingredients for hot melt adhesives, sealants and coatings at their plant in Texas. The company foresees continuing growth of demand for these resins which are offered in more than 20 grades.

### Expanded emulsion production capacity

Harlow Chemical Co. Ltd, a company owned jointly by Hoechst UK Ltd and Revertex Ltd, are expanding their capacity for the production of synthetic resin emulsions at their plant at Stallingborough, South Humberside. A new plant of 15,000 tonnes p.a. capacity has been opened, and there are plans to build a pressure plant for the production of vinyl acetate/ethylene copolymer emulsions in the future.

### New products

#### New paint mixing machine

Inmont Ltd has announced the availability of the new Euromatic 200 paint mixing machine which is designed to provide up to 30,000 colour matches from 40-50 basic colours. The Euromatic uses the Inmont Tintometer mixing unit which allows quantities of paint down to a quarter of a litre to be mixed, and it is claimed that any colour used on cars dating back to 1948 can be matched by this system.

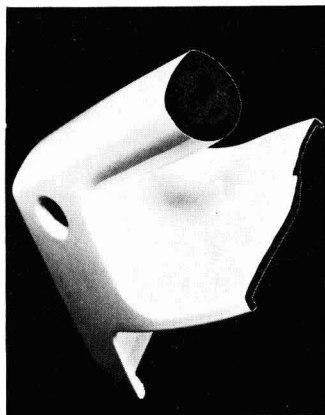
#### New analytical systems from IBM

The Instrument Systems Group of IBM United Kingdom Ltd has announced the introduction of two new analytical systems which combine the precision of spectrophotometry with the speed of digital computing techniques. The IBM 7841 Textile Colour Analyser and the IBM 7842 Coatings

Colour Analyser, designed to meet the specific needs of the textile and paint industries, are extensions of some of the instrument technology developed and used in IBM's own plants and laboratories; the speed and accuracy are achieved in both instruments by the integration of advanced optical measurement with digital processing. Through a series of questions and answers, called prompting routines, the operator can use the colour analysers in many applications including colour matching, production and laboratory adds, dye and pigment analysis, shade sorting etc.

#### Durable coatings

Electric irons, produced by Hotpoint Ltd, are being powder coated with an epoxy thermoset coating developed by Drynamels Ltd. The problem of coating a non-conductive material was overcome by an electrostatic leakage to earth mechanism, and as shown in the picture, when the handle is smashed by a hammer blow, the epoxy thermoset powder coating does not even chip, but follows the line of the break perfectly, demonstrating the coating's durability.



The smashed handle of an iron, showing the clean line of break of the epoxy powder coating.

#### Asbestos replacement

Owing to more stringent handling procedures which have recently been applied to the use of asbestos, Lawrence Industries have introduced Attagels as suitable substitutes. The chainlike structure of Attagel gives it similar properties to asbestos fibre without the associated hazards, and can also impart flexibility, strength, insulating and extending properties to both dry powder and liquid systems.

#### Batch counter

The BC 11 Batch Counter is a new addition to the range of electronics in DIN sized cases from AOT Flowmeters Ltd. The unit enables liquids to be batched using signals from turbine-type flowmeters.

#### Rupture disks

LOBA (Industrial Products) Ltd has announced the availability from their Instrument Division of FIKE rupture disks, which are designed to provide a controlled

relief with predictable characteristics from vacuum to 30,000 lb/sq. inch Fitted into a vessel or pipeline, they act in an analogous manner to an electrical fuse, rupturing at a predetermined pressure to protect more delicate or more expensive equipment from damage in an emergency.

#### New electromagnetic flowmeter

A new electromagnetic flowmeter, designated the Brooks-Miag Series 7800 Flowmeter, incorporating both flow transmitter and signal converter in one compact assembly and operating with a standard accuracy of  $\pm 0.5$  per cent of maximum flowrate has been developed by Brooks Instruments. It can be mounted directly in pipelines without restricting flow, and the combination of the transmitter and converter in one unit eliminates the need for special shielded connecting cables which can pick up noise.

#### New Beetle resin

A new Beetle alkyd resin, BA 549, designed primarily for use in low-bake systems, is now available from BIP Chemicals Division, and may be used in combination with any one of a large number of Beetle melamine resins. Such systems cure well at temperatures around 90-95°C and then continue to post cure at room temperature for several weeks. The new resin has excellent colour stability and may be used for general purpose industrial stoving finishes, in cold cure wood finishes and in fast cure finishes for paper and other substrates.

#### Minitest coating thickness gauge

Surfatest has announced the introduction of the new Type N.50 addition to the Minitest range of coating thickness gauges, which has been designed specifically for the measurement of anodic films on aluminium and other thin coatings on non-ferrous metals. The battery operated instrument is capable of accurately measuring coatings down to a thickness of 5  $\mu\text{m}$ .

#### New vibrating discharger

Triton Engineering Co. Ltd has available the new Triton Discharger, an open frame raised vibrating unit specifically designed for speeding and ensuring complete emptying of central base discharge bulk containers or similar vessels. The unit is claimed to overcome the problems caused by static build-up.

#### Microprocessor-based flow control

Jiskoot Autocontrol Ltd has announced the availability of the Micro-Matic J-R8/3 which supersedes the J-R8/2. It is a highly versatile stream instrument for flow control and monitoring applications in process engineering and it is claimed that the instrument can undertake operations which would normally require as many as ten conventional instruments. The capabilities of the J-R8/3 include mass flow computation, automatic temperature compensation, batching and in-line blending, flow computation and control and closed-loop three term control.

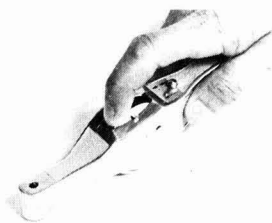
#### Adhesive guns

Packaging Aids Ltd has available two new models of their Flo Fix Minimatic, the models LD and HDE, designed for carton sealing and light duty bonding applications. These light duty hot melt adhesive dispensing guns have found use in the paint

manufacturing industry, and the new models which have been simplified, reduce the cost of this type of gun considerably.

#### New coating thickness gauge

The Elcometer 211 is the latest development in the Inspector magnetic coating thickness gauges from Elcometer Instruments Ltd, and incorporates the unique ability to lock the instrument automatically when a reading is taken, or to leave it moving freely without restriction.



The Elcometer 211, the latest addition to the Inspector range of coating thickness gauges.

#### Conferences, courses etc

##### Electronics for printing

The Technical Training Board of the Society of British Printing Ink Manufacturers will hold the TTB Annual Lecture on Monday 13 November at the Royal Institution, when Mr R. D. Tibbitts of Crosfield Electronics Ltd will talk on 'Electronics for printing'.

##### New BSI Standards

The British Standards Institution has issued the following new standards: *BS 1851* - Titanium pigments for paints; *BS 662, Pt 2* - Carbon disulphide for industrial use. Sampling and methods of test; *BS 5598, Pt 1* - Methods of sampling and test for halogenated hydrocarbons. Sampling of liquid products; *BS 303* - Lead chrome green pigments for paints; *BS 3900* - Methods of test for paints. *Part A13* Rapid test for determination of danger classification by flashpoint. *Part A14* Rapid test for determination of flashpoint. *Part C8* Print free test. *Part D1* Visual comparison of the colour of paints (revised); *BS 3145* - Laboratory pH meters; *BS 3900* - Methods of test for paints. *Part A6* Flow cups; *BS 1733* - Flow cups and methods of use (*draft*).

##### Attagel 50 leaflet

Lawrence Industries has available a new leaflet entitled 'Attagel - a unique mineral thickener', which describes the way in which this processed Attapulcus clay can impart thickening and thixotropy to a wide variety of organic and water-based systems. The leaflet suggests pregel formulations for various solvent systems using Attagel 50 as a substitute for modified Bentonite and cellulose organic thickeners.

##### Adhesives directory

A. S. O'Connor & Co. Ltd has published the 1978 edition of the Adhesives directory which contains a complete list of UK adhesive suppliers together with charts and a checklist for the selection of the correct type of adhesive.



# OCCA-31 Exhibition

Alexandra Palace, London, 3-6 April 1979

The international focal point  
for the  
surface coatings industries

## Good support for OCCA-31 from organisations in many countries

### Arrangements for OCCA-31

The Exhibition Committee announces that the thirty-first annual exhibition of raw materials, plant and equipment for the paint, printing ink, colour, polymer, adhesive and allied industries organised by the Association will be held at Alexandra Palace, London N22 from 3-6 April 1979.

The aim of the Exhibition is the presentation of technical and commercial information relating to advances in the surface coatings industries. The Committee stipulates that a technically trained person who has knowledge of the products displayed be available on the stand throughout the Exhibition.

Whilst the Committee naturally encourages the showing of new products, it does not stipulate that a new product has to be shown each year, since it fully appreciates that this is not possible. Accordingly, the Committee draws attention to the fact that new technical data on existing products is regarded as acceptable matter.

### Motif for the Exhibition

The motif, designed by Robert Hamblin, emphasises the unique aspect of the OCCA Exhibitions, which annually provide an international focal point for the surface coatings industries. In 1978, exhibitors were drawn from 16 countries and visitors from over 50 countries. The colours of the motif shown on the outside cover will be carried throughout the publicity leading up to the Exhibition. The two main colours of the motif, green and yellow, will be incorporated on the facias of the stands and it is intended to organise complementary



Visitors to the OCCA-30 Exhibition came from over 50 countries

floral displays in the Exhibition Hall. The use of these colours will create a pleasing contrast as visitors move from corridor to corridor at the Exhibition, as the green colour will be used from north to south and the yellow colour from east to west.

### Dates and hours of opening

The Exhibition will be open as follows:

Tuesday 3 April ..	09.30 to 17.30 hrs.
Wednesday 4 April ..	09.30 to 17.30 hrs.
Thursday 5 April ..	09.30 to 17.30 hrs.
Friday 6 April ..	09.30 to 16.00 hrs.

### Invitation to Exhibit

Copies of the Invitation to Exhibit have been despatched to companies and organisations in the UK and overseas which have shown at previous OCCA Exhibitions or have requested information for the first time for the 1979 Exhibition. Completed application forms for stand space must be returned to the Director & Secretary of the Association not later than 31 October 1978.

Any organisation wishing to receive details of OCCA-31 should write to the Director & Secretary of the Association for a copy of the Invitation to Exhibit.

The interest shown in the OCCA-31 Exhibition as a direct result of the highly successful OCCA-30 Exhibition held in April this year has been considerable, and already companies have asked for larger stands than they have had in previous years. Additionally, several companies who have not previously shown at OCCA Exhibitions as well as some who were not able to be present at OCCA-30 have contacted the Association requesting that sites be reserved for them.

The Exhibition Committee was particularly pleased to see the large number of exhibits at OCCA-30 from companies new to the Exhibition, both from the UK and many overseas countries, and this emphasises the continuing importance of this annual Exhibition to the world surface coatings industry and demonstrates its international character. The number of stands at OCCA-30 was larger than at the Exhibition for several years, and the number of companies was also greater. It will be appreciated that an exhibitor may request a stand of the size to suit his requirements, and thus the Committee points out that it is possible for organisations to demonstrate their products in a cost effective manner; however, there is no restriction on the maximum size of stand an exhibitor may

request, and exhibitors are now permitted to serve alcoholic refreshments to their visitors on the stands.

### Admissions at OCCA-30

Visitors to the OCCA-30 Exhibition are known to have come from over 50 overseas countries, and admissions by season ticket of over 10,000 were recorded at the entrance during the four days.

All Members of the Association receive a free season admission ticket with their copy of the Official Guide, and organisations exhibiting receive complimentary admission tickets to distribute to their customers. In addition, many trade associations are also sent tickets for distribution to their members. Thus, many visitors to the Exhibition have season admission tickets provided in advance.



Admissions by season ticket of over 10,000 were recorded at OCCA-30

However, an analysis\* of the tickets purchased at the entrance to the hall, sold mainly to visitors who have come as a result of the Association's widespread publicity rather than having been invited by exhibitors, shows that 34 per cent of these visitors came from overseas, with a significant proportion coming to the Exhibition from outside Europe. Particularly impressive amongst these visitors from overseas was the high proportion of top personnel: 61 per cent of them were managers, directors or owners of companies, with a 55/45 split between technical and commercial people.

With visitors from the United Kingdom, the split between technical and commercial personnel was 64/36; again there was a

## Alexandra Palace



Alexandra Palace stands high on the hills of north London, commanding a panoramic view of the city skyline. The Association has full use of the facilities at Alexandra Palace during the period of the Exhibition, which include a restaurant, bars, a cafeteria and a private exhibitors' bar. Another facility which is of considerable benefit to those travelling to the Exhibition by car is the ample free car parking space within the Palace grounds.

For visitors travelling to the Exhibition on the underground system, the Association will once again be operating a free bus shuttle service to and from the Exhibition from *Wood Green* station on the Piccadilly Underground Line. The extension of the Piccadilly Line to the Heathrow Central terminal, opened in late 1977, now provides a direct link for travellers arriving at the airport both to central London and to Wood Green station and the bus shuttle service to the Exhibition.

### Improvements at Alexandra Palace

A comprehensive refurbishment of the facilities at Alexandra Palace was started in July 1978, and already the floor of the Great Hall, in which the Exhibition is held, has been re-surfaced and the West Corridor has been redecorated. The work on the exterior of the building is to be completed and the restaurants, bars and the walls of the Great Hall are also to be redecorated. These improvements are scheduled to be completed by the late summer this year.

Both Exhibitors and visitors will welcome these improvements which will add to the pleasantness of the setting for this international focal point for the surface coatings industries.



The west side of Alexandra Palace

large proportion of senior management, although there was also a strong representation of section heads/group leaders and chemists.

These figures indicate the great value to organisations of exhibiting their products and developments at OCCA Exhibitions, which continue to attract each year large numbers of interested visitors from all over the world. The Exhibition provides a forum where exhibitors can discuss their products with the senior executives and technical personnel of many organisations whom they would not otherwise be able to contact, or to whom it would be prohibitively expensive to send representatives.

### Information in foreign languages

As in previous years, the Association will be circulating information leaflets in six languages which will contain application forms for those wishing to purchase copies of the *Official Guide* and season admission tickets before the Exhibition. Interpreters will once again be in attendance at the Information Centre at the Exhibition to assist foreign exhibitors and visitors with their queries.

### Hotel accommodation

In order to facilitate the booking of hotel accommodation by visitors, the Grand Metropolitan Hotels Ltd will again be publishing a special leaflet for OCCA-31, which will be distributed in all copies of the *Journal* sent overseas in December.

### Official Guide

This unique publication contains descriptions of all companies and their exhibits at the Exhibition and is issued to each member of the Association at home and abroad as well as to all visitors to the Exhibition with their admission tickets. It is published several weeks in advance of the dates of the Exhibition to allow visitors the maximum opportunity to plan the itinerary of their visits. In 1978, for the first time, the *Official Guide* contained a chart classifying the products on show into the various types, and it is intended to produce a similar chart for the *Official Guide* to OCCA-31. This chart is invaluable to visitors, especially those who have only a limited amount of time available, as it provides a quick, easy reference of all the companies present who are displaying the products in which they are interested.

### Advertising facilities

Advertising space is available in the *Official Guide*, both to companies who will be exhibiting at the Exhibition, and also to other organisations. This important publication is constantly referred to both before the Exhibition and afterwards as a convenient record of the latest developments in the industry. Consequently, organisations wishing to take advertising space in the Guide should book their requirements as soon as possible in order to ensure a prominent position. Details of the advertising rates and media data are available from Mr D. M. Sanders at the Association's address.

\*Sample of 1600 completed tickets taken from those purchased at the entrance to the Exhibition.

## Report of Council Meeting

A meeting of the Council of the Association was held on 5 July 1978 at the Great Northern Hotel, Kings Cross, London, NI at 2 p.m. There were 30 members present.

In the unavoidable absence of the President (Mr A. McLean), owing to the illness of his father, it was agreed that Mr F. Sowerbutts (President 1967-1969 and Representative, Auckland Section) should take the Chair.

On behalf of the President, Mr Sowerbutts welcomed all members who were serving on Council for the first time or had returned after a previous period of service. It was reported that the three Members elected at the Annual General Meeting on 21 June were:

Mr J. R. Taylor  
Mr C. H. Morris  
Mr J. D. W. Davidson

and a report was received on the Luncheon and Lecture, arranged by the London Section, at the Piccadilly Hotel, London, WI, which had preceded the Annual General Meeting. The dates of the Council Meetings for the forthcoming session were agreed and the appointment of members to serve on Committees of Council and to represent the Association on other organisations was confirmed.

Reports were received on the progress made for the Association's Exhibition (OCCA-31, 3-6 April 1979) and the Stratford-upon-Avon Conference (20-23 June, 1979).

Details of the number of members in arrears with their 1978 subscriptions were reported and Council noted with satisfaction that the total was considerably smaller than at the comparable date in 1977.

Council was pleased to learn that a paper would be presented on behalf of the Association at the F.S.C.T. Convention in Chicago (1-3 November) by Mr J. C. Bax on "New concepts in the formulation of gloss latex paints".

It was reported that bound copies of reprints from the *Journal* of the papers given at the Second International Symposium on Ultraviolet Polymerisation organised by the Newcastle Section in September 1977 would be available in the autumn. Reports were received on Section activities at home and overseas. Authority was given for the printing of the South African Division Rules and the Council extended its best wishes to the New Zealand Division for the success of their Convention at Rotorua (27-30 July).

A suggestion from the Manchester

Section Committee that a car rear window sticker be made available for recruitment and publicity purposes was approved. A pilot scheme would be operated at first by the Manchester Section and other Section Chairmen would advise the Director & Secretary if they wished to have samples for their Sections.

Brief reports on liaison matters arising from discussions at the FATIPEC Congress in Budapest (4-9 June) and the visit of the President (Mr J. Oates) and the Executive Vice-President (Mr F. Borelle) of FSCT to London, where they attended the Association's AGM Luncheon and Lecture, were given.

It was reported that many appreciative letters had been received from guests attending the 60th Anniversary Celebrations (11-12 May 1978).

Council accepted unanimously the recommendation of the President's Advisory Committee that a Commendation Award be conferred upon Mr L. J. Brooke, who had completed many years continuous service on the Bristol Section Committee in one capacity or another.

There being no further business, the meeting passed a vote of thanks to Mr Sowerbutts for taking the Chair and he then declared the meeting closed at 3.35 p.m.

## Hull Section

### Dinner and Dance

The Hull Section Dinner and Dance will be held on Friday 6 October 1978 at the Willerby Manor Hotel, Willerby, near Hull. Tickets price £7.50 (inc. VAT) are available from the Hon. Social Secretary, Mr A. R. Van Spall, Jusrite, 5 Middle Garth Drive, South Cave, Brough HU15 2AY.

## Bristol Section

### Commendation Award. Mr D. N. Fidler

The Chairman of the Bristol Section, Mrs E. N. Harper, presented a Commendation Award to Mr D. N. Fidler during the Bristol Section Annual Dinner Dance on Friday 31 May. Mr Fidler has recently relinquished the post of Honorary Programmes Secretary of the Section to become

Chairman Elect, and has previously been Assistant Secretary and the Secretary of the Section from 1964 to 1977. To mark the occasion, the Chairman also presented Mr Fidler with record and book tokens contained inside a copy of the latest edition of the Introduction to Paint Technology, signed by many of his friends in the Bristol Section.

In his speech of thanks Mr Fidler remarked that 'Having listened to all the lectures over the past years, I will now be able to understand what they were all about.'

### Presentation to Mr L. J. Brooke

During the same evening, the Chairman presented on behalf of members of the Bristol Section, a gift of six Georgian crystal sherry glasses to the past Chairman, Mr L. J. Brooke.

Mr Brooke who has completed 25 years continuous service to the Section, has during this period been Secretary for seven years,

Treasurer for seven years, and has twice been Chairman.

Mr Brooke expressed his gratitude to his fellow members for their most acceptable gift.

J.R.T.

### News of Members

Mr D. S. Medcalf, an Associate Member attached to the Irish Section, has been appointed a Director of ICI (Ireland) Ltd after 30 years with the firm.

Mr M. H. Prigmore, Representative on Council of the Thames Valley Section, has joined the Powder Coatings Division of the Valentine Varnish & Lacquer Co. Ltd.

## Register of Members

The following elections to membership have been approved by Council. The Section to which each new Member is attached is given in italics.

### Ordinary Members

- BETTISON, IAN DAVID, 5 Pokaka Street, Upper Hutt, New Zealand. (*Wellington*)
- EL-BARADIE, HUSSNY YOUSSEF FAHMY, MSc, PhD, Chemistry Department, Faculty of Education, King Abdul-Aziz University, Mecca, Saudi Arabia. (*General Overseas*)
- GOODALL, CHRISTOPHER, LRIC, Harlands of Hull Ltd, Land of Green Ginger House, Anlaby, Hull. (*Hull*)
- GOUGH, GERARD, Bayer (Ireland) Ltd, Dun Laoghaire, Co. Dublin. (*Irish*)
- GRECO, FRANCO PIETRO, Fergusson's Paints (Pty) Ltd, PO Box 12050, Jacobs 4026, South Africa. (*Natal*)
- GREENE, PETER WILLIAMS, 5 Winton Road, Orpington, Kent BR6 7AL. (*London*)
- HEPERS, KONRAD JOHN, British Paints (NZ) Ltd, PO Box 19020, Auckland 7, New Zealand. (*Auckland*)
- LINDSAY, BARRY GORDON, MSc, Mobil Oil (NZ) Ltd, PO Box 1709, Auckland, New Zealand. (*Auckland*)
- MURRAY, BRIAN RUSSELL, 15 Lynmore Drive, Manurewa, New Zealand. (*Auckland*)
- PARKER, RAYMOND, LRIC, Plot 530 Stonebridge Drive, Selwood Park, Frome, Somerset. (*Bristol*)
- WILBY, SHAUN PATRICK, 22 Blakeridge Lane, Batley, West Yorkshire WF17 8PD. (*West Riding*)

WILLIAMS, BRYNLEY GLYN, BSc, Dow Corning (NZ) Ltd, PO Box 15404, Auckland, New Zealand. (Auckland)

WILLIAMSON, GYNNIE, Usher Walker Ltd, Canal Street, Kirkintilloch, Glasgow. (Scottish)

WRIGHT, PHILIP CHARLES, 28 Hereford Road, Oldbury, Warley, West Midlands B68 0QQ. (Midlands)

#### Associate Members

BUDDEN, NIGEL KEITH, Neil Cropper & Co. Ltd, PO Box 9, Auckland, New Zealand. (Auckland)

CLATWORTHY, GARY PHILIP, Box 37-408, Auckland, New Zealand. (Auckland)

HENDERSON, JOHN HANDLEY, 50 Ladythorn Road, Erenhall, Cheshire. (Manchester)

HUDSON, JOHN TREVOR, Hardie Trading Co. NZ Ltd, PO Box 1367, Auckland, New Zealand. (Auckland)

LEVSHIN, PETER, 243 Great North Road, Grey Lynn, New Zealand. (Auckland)

VERGHESE, SEBASTIAN, Protectind Ltd, Unit 1, 702A Whinfield Drive, Aycliffe Industrial Estate, Co. Durham. (Newcastle)

## Forthcoming Events

Details are given of Association meetings in the United Kingdom and Ireland up to the end of the month following publication and in other parts of the world up to the end of the second following publication.

### September

#### September

*Auckland Section:* Talk and factory inspection—N.Z. Starch Products Ltd, Te Papapa. *Details to be announced.*

#### September

*West Riding Section:* West Riding Chairman's Golf Trophy at the Knaresborough Golf Course. *Details to be announced.*

#### Tuesday 5 September

*West Riding Section:* 'Defoaming agents; the theory and application with regard to the paint industry' by Mr R. W. Harrison of Diamond Shamrock Chemicals (UK) Ltd, at the Mansion Hotel, Roundhay Park, Leeds 8 at 7.30 p.m.

#### Friday 8 September

*Thames Valley Section:* Medieval evening at Great Fosters, Egham. *Details to be announced.*

#### Wednesday 13 September

*Manchester Section:* Golf Tournament at the Stockport Golf Club. *Details to be announced.*

#### Thursday 14 September

*Midlands Section—Trent Valley Branch:* 'Cathodic protection' by D. E. Marlborough of Metal & Pipeline Endurance Ltd, to be held at the Crest Hotel, Pastures Hill, Littleover, Derby commencing at 7.00 p.m.

#### Friday 15 September

*Irish Section:* 'The theory and practice of pigment dispersion' by Dr W. Carr of Ciba-Geigy, at the Clarence Hotel, Dublin at 8.00 p.m.

*Manchester Section:* Student Seminar 'Emulsion paints' at the Woodcourt Hotel, Sale, Cheshire. *Details to be announced.*

#### Thursday 21 September

*London Section:* 'Marketing with reference to the developing countries and the EEC' by Mr R. I. Farr, Cowan Colours Ltd, at the 'Princess Alice', Romford Road, E7 at 6.15 p.m.

#### Friday 22 September

*Midlands Section:* Ladies' Night. Dinner and Dance at the Botanical Gardens,

Birmingham. *Details to be announced.*

#### Thursday 28 September

*Midlands Section:* 'Foaming in aqueous media' by T. G. Palmer of Bevaloid Ltd, at the Calthorpe Suite, County Ground, Birmingham at 6.30 p.m.

#### Friday 29 September

*Bristol Section:* 'The development of horizontal milling, with particular reference to the Dyno Mill' by Mr D. I. R. Kerr of Glen Creston Machinery Ltd, at the Royal Hotel, College Green, Bristol at 7.15 p.m.

### October

#### October

*Auckland Section:* 'Hot method adhesives and coatings' by Mr D. Reid of Petersons Chemicals. *Details to be announced.*

#### Monday 2 October

*Hull Section:* 'The practical problems of painting and maintaining large industrial plant' by D. A. Bayliss of BIE Anti-Corrosion Ltd. Joint meeting with the Institution of Chemical Engineers, at the Humber Bridge Hotel, Barton, South Humberside at 6.45 p.m.

#### Tuesday 3 October

*West Riding Section:* 'Instrumental colour control in the paint industry' by Mr R. P. Best of Instrumental Colour Systems Ltd, at the Mansion Hotel, Roundhay Park, Leeds 8 at 7.30 p.m.

#### Thursday 5 October

*Newcastle Section:* 'Solvent recovery for the surface coatings industry' by Mr I. Smallwood of Fraser McNaughton Ltd, at St. Mary's College, Elvet Hill Road, Durham at 6.30 p.m.

#### Friday 6 October

*Hull Section:* Annual Dinner Dance, to be held at the Willerby Manor Hotel, Willerby, near Hull.

#### Thursday 12 October

*Midlands Section—Trent Valley Branch:* 'Coil coatings' by Dr Gilmore of Conway Coatings Ltd, at the Crest Hotel, Pastures Hill, Littleover, Derby at 7.00 p.m.

*Scottish Section:* 'The practical problems of painting and maintaining large industrial plants' by D. Bayliss of BIE

Anti-Corrosion Ltd, at the Albany Hotel, Glasgow, at 6.00 p.m.

*Thames Valley Section:* 'Coatings for wood', One day meeting at Building Research Establishment, Princes Risborough. *Details to be announced.*

#### Friday 13 October

*Manchester Section:* 'Theory versus practice of dispersion' by Dr W. Carr of Leeds University at the Manchester Literary & Philosophical Society, George Street, Manchester, at 6.30 p.m.

#### Tuesday 17 October

*London Section:* Afternoon visit to the Metropolitan Police Forensic Science Laboratory, Lambert Road, London SE1 at 2.30 p.m.

#### Wednesday 18 October

*London Section:* 'Finishes and materials for window frames' by Mr P. Whiteley of Building Research Establishment, at Rubens Hotel, Buckingham Palace Road, SW1 at 7.00 p.m.

#### Thursday 19 October

*Midlands Section:* 'Coil coating' by Mr E. Sharpe of Merritts Ltd, at the Calthorpe Suite, County Ground, Birmingham at 6.30 p.m.

#### Friday 20 October

*Irish Section:* 'Aqueous based printing inks' by Mr R. Millard of Harlow Chemical Co. Ltd, at the Clarence Hotel, Dublin at 8.00 p.m.

*Manchester Section:* Annual Dinner Dance at the Piccadilly Hotel, Manchester. *Details to be announced.*

#### Friday 27 October

*Bristol Section:* 'The refinishing of motor vehicles' by Mr D. E. Sellen of Berger Paints, at the Royal Hotel, College Green, Bristol at 7.15 p.m.

*London Section:* Ladies' night, to be held at Selsdon Park Hotel, Sanderstead, Surrey, at 7.00 for 7.30 p.m.

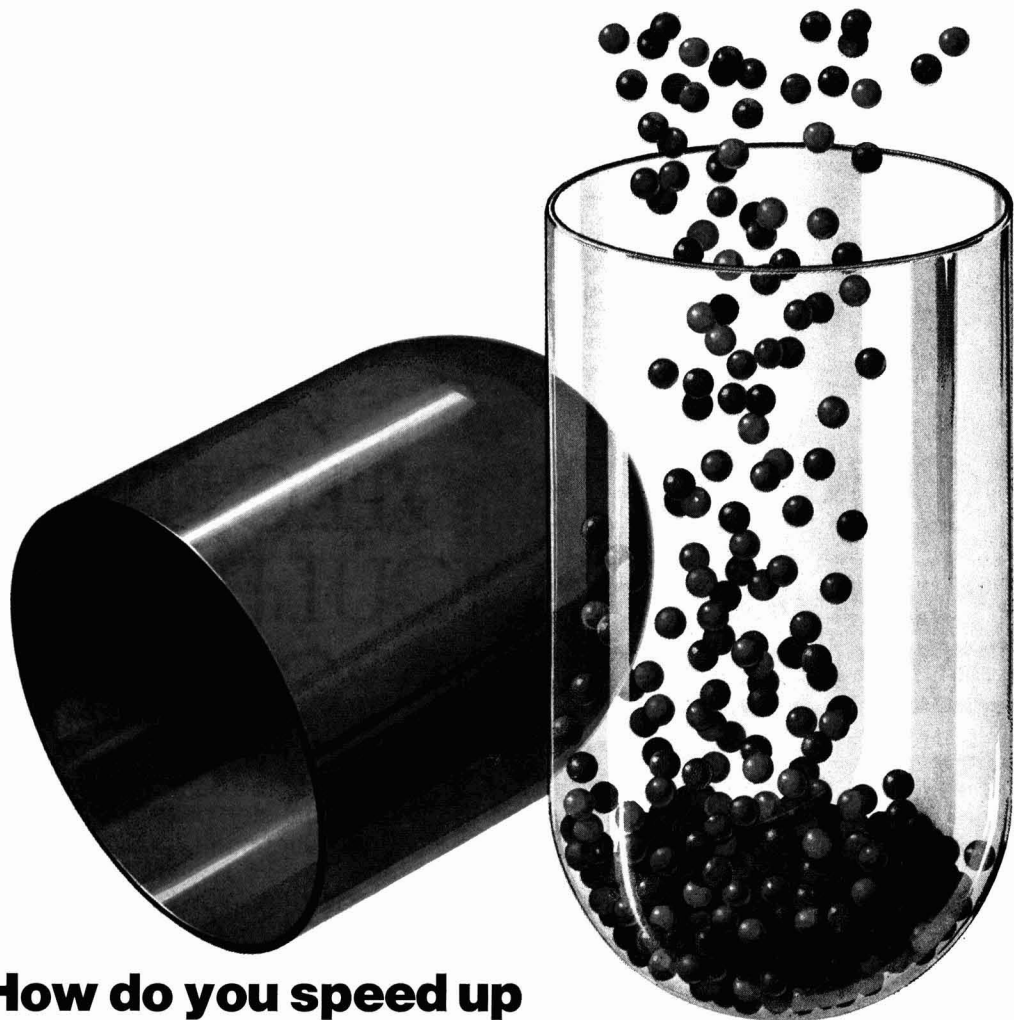
*Scottish Section—Eastern Branch:* Skittles match at the Civil Service Club, Marine Drive, at 7.00 for 7.30 p.m.

### November

#### November

*Auckland Section:* Talk and inspection of the Water Treatment Plant, Auckland Regional Authority at Titirangi, by Mr D. Payne.





## How do you speed up filling according to formula?

Mettler PL3001 and PL301 electronic balances with built-in net total display feature can effect great time savings when weighing in according to formula. This feature allows the operator to display intermediary totals whenever desired. It allows quick comparison with the formula, reduces risk of error if mixing is interrupted, and eliminates calculations. These are ideal balances for pharmaceutical companies and others involved



with formula compounding. — Mettler helps solve problems in analytical laboratories and on the production floors of industry. We market a variety of weighing and measuring instruments. All of them made with world-renowned Mettler craftsmanship. All of them backed by a worldwide team of service specialists who can be there when you need them. Mettler — instruments and people you can depend on.

## Depend on Mettler for the answer.

*METTLER*

Electronic balances and weighing systems · Thermoanalytical instruments · Automatic titration systems · Laboratory automation

6262.72

**Gallenkamp**

Exclusive UK distributors: A. Gallenkamp & Co. Ltd.

P.O. Box 290, Christopher Street, London EC2P 2ER, Tel. 01-247 3211 · Branches at Birmingham, East Kilbride, Widnes, Stockton-on-Tees



# QUALITY PROTECTIVE COATINGS SHOULD HAVE ONE THING IN COMMON.

High quality paints demand high quality resins. That's why Shell Chemicals are the leading suppliers of epoxy resins to the world's paint industry.

Our Epikote epoxy resins are helping to produce tough primers, marine paints and protective coatings to stand up to every environment.

We don't stop with epoxy resins. Cardura resins are being used to

make tough industrial finishes, and VeoVa forms the basis of latices for the best emulsion paints.

Shell Chemicals quality of manufacture is backed by the research and technical support groups based at our Polymers Centre in Amsterdam.

Your Shell company will be happy to tell you how the quality of Shell resins can help you make a quality paint.

**EPIKOTE: BETTER RESINS MAKE BETTER PAINTS.**



**Shell Chemicals**

# SHELL CHEMICALS FOR INDUSTRY

## Resins

Epikote resins and Epikure curing agents, Cardura E10 and VeoVa 10 resin intermediates.

## Elastomers

Cariflex TR thermoplastic rubber, Cariflex SBR, BR and IR.

## Thermoplastics

Shell Polypropylene, Carlona low density polyethylene, Shell polystyrene\*, Styrocell expandable polystyrene, Carina polyvinylchloride\*

## Urethane Chemicals

Caradol polyols and Caradate isocyanates.

## Base Chemicals

Ethylene, propylene, butadiene, dicyclopentadiene, benzene, toluene, solvent xylenes, ortho xylene, para xylene, cumene, styrene monomer, sulphur, Versatic 10, Dutrex and Shellflex grades, naphthenic acids, premium needle coke.

## Industrial Chemicals

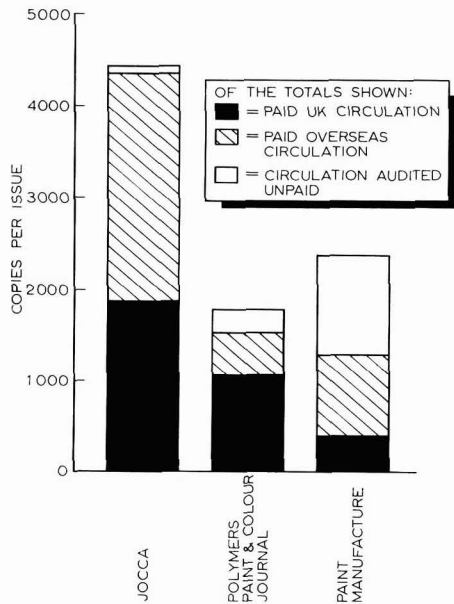
Chemical solvents, phenol, hydrocarbon solvents, detergent alkylates and alcohols, ethylene oxide, glycols and derivatives, plasticisers and plasticiser alcohols, epichlorhydrin, glycerine.

## Speciality Chemicals

Fine chemicals, antioxidants, catalysts, mining and textile chemicals, Apiezon oils, greases and waxes, additives for lubricating oils and fuels.

\*available in certain areas.

## Comparison of circulations of U.K. publications to the paint, printing ink and allied industries



(Reference Audit Bureau of Circulations Reviews, Jan-Dec 1977)

For full details of advertising in this, and other Association publications, contact D. M. Sanders, Assistant Editor

## Journal of the Oil and Colour Chemists' Association (JOCCA)

Priority House, 967 Harrow Road, Wembley, Middx. HA0 2SF, England

Telephone: 01-908 1086

Telex: 922670 (OCCA Wembley)



Shell Chemicals

# CURRENT PUBLICATIONS

**New fourth  
edition now  
available**



The Introduction to Paint Technology, of which 18,000 copies have already been sold, forms an excellent introduction to the whole field of surface coatings and related technologies. The fourth edition contains the important addition of a glossary of the terms used in the book together with explanations of their derivations, as well as the completely revised and updated text.

**Price £5.00** (Registered Students of the Association £2.50) **Prepayment only.**

**OIL AND COLOUR CHEMISTS' ASSOCIATION**  
Priory House, 967 Harrow Rd., Wembley HA0 2SF

*Special Reduction!*

## TEN-YEAR CONSOLIDATED INDEX

of Transactions  
and Communications

**1966-1975**  
**Volumes 49-58**

The remaining copies of the Consolidated Index are offered at a specially reduced rate for a limited period only.

The special rate will be:

**£2.00 to non-Members; £1.00 to Members**

**AVAILABLE (prepayment only) from:**

**OIL AND COLOUR CHEMISTS' ASSOCIATION**  
Priory House, 967 Harrow Rd., Wembley HA0 2SF

**UV** Ultraviolet Polymerisation and the surface coatings industry  
**polymerisation**

The bound papers from the two recent symposia are available at a special reduction: **Price £10.00 for both booklets.**

**UV2**

## Paint Technology Manuals Works Practice

This publication, which is of great use both to the practical man within the industry and the student entering the industry, is concerned with the practical aspects of making paints. As very little has been published on this subject, a fairly broad coverage is attempted including factory layout and organisation, paint and media manufacturing processes, legal aspects and safety precautions.

**Price: £3.00**

## Convertible Coatings

The second edition of Convertible Coatings, published in 1972, is invaluable to those dealing with this aspect of the industry, and a few copies are still available.

**Price: £7.50** Published by Chapman & Hall Ltd on behalf of the Association.

## Biennial Conference PREPRINTS

The Association organises an international Conference every two years and preprints of the papers are prepared for delegates. A strictly limited number of the following are available to those who wish to have the complete bound sets of papers.

**1977 Eastbourne** *The conservation of energy, materials and other resources in the surface coatings industries.* Fourteen papers presented. **Price: £5.00**

**1975 Scarborough** *Performance of surface coatings—does reality match theory?* Seventeen papers presented. **Price: £5.00**

**1973 Eastbourne** *Towards 2000.* Sixteen papers presented. **Price: £5.00**



# QUALITY CONTROL APPARATUS

● VISCOSITY

● GLOSS

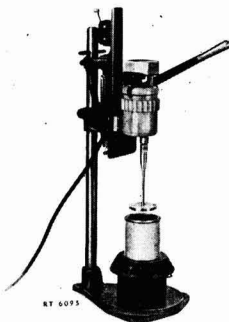
● DRYING TIME

● COLOUR

● HARDNESS

● OPACITY

● IMPACT



● ABRASION

● FILM APPLICATION

This range of viscometers, available as electric models or air driven models for use in hazardous areas, provides the means of rapid determinations within the ranges up to 5 poise, 15 poise, 65 poise and 340 poise. Simple to use, and easy to clean.

## SHEEN INSTRUMENTS (SALES) LIMITED

9, SHEENDALE ROAD, RICHMOND, SURREY TW9 2JL Telephone: 01-940 0233 and 1717  
CABLE: SHEENINST RICHMOND SURREY

### BOOK ORDER FORM (PREPAYMENT ONLY)

To: The Director and Secretary,  
Oil & Colour Chemists' Association,  
Priory House,  
967 Harrow Road,  
Wembley, Middx.,  
HA0 2SF  
England.



Date.....

Please send me copies of the books as listed below:

.....  
.....  
.....  
.....

I enclose remittance of £ (US \$) ..... to cover the cost. (Prepayment only)

NAME .....

ADDRESS TO WHICH THE BOOKS SHOULD BE SENT:

.....  
.....  
.....

In order to avoid unnecessary delay please enclose correct remittance with your order.

## CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of £4.00 per cm. Advertisements for Situations Wanted are charged at £1.00 per line. A box number is charged at 50p. They should be sent to D. M. Sanders, Assistant Editor, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF. JOCCA is published EVERY month and Classified Advertisements can be accepted up to at least the 12th, and in exceptional circumstances the 20th of the month preceding publication. Advertisers who wish to arrange for an extension of the copy deadline should contact the Assistant Editor, D. M. Sanders, at the address given above (telephone 01-908 1086, telex 922670 OCCA Wembley).

## APPOINTMENTS VACANT

## INDUSTRIAL CHEMIST

A vacancy exists for an industrial chemist or coating technologist to take an active lead of a small sub-section responsible for the physical testing and environmental testing of coated products. Applicants should have 3 to 5 years experience in the development or in the testing to specifications of industrial finishes, and preferably will possess H.N.C. or G.R.I.C. minimum qualifications. The successful applicant will be responsible to a Senior Chemist. Duties will require co-operation with product development sections, and with Production and Sales departments. He/she will be expected to participate in supplier and customer technical services.

We are an international company engaged in the manufacture and erection of specialised steel and plastic building materials on a large scale.

Salary will be fully competitive; contributory pension scheme with life assurance cover.

Please write or telephone for application form to:—

The Secretary,  
Personnel Department,

**H.H. Robertson (U.K.) Limited**  
Ellesmere Port, South Wirral, L65 4DS  
Tel: 051-355 3622



## SITUATIONS WANTED

**Young paint chemist** in middle thirties, with Degree, desires employment in Middle East countries, Iran on contract basis, can handle production as well as customer service/research. Several years' experience in decorative and industrial coatings, trade sales.

Box No. 461

## OCCA Conference 1979

'The challenge to coatings in a changing world'

20-23 June 1979

Stratford-upon-Avon

The next biennial conference of the Association will be held at the Stratford Hilton Hotel, Stratford-upon-Avon, from Wednesday 20 to Saturday 23 June 1979.

Details of the papers to be presented and biographies of the lecturers will be published in the *Journal* later this year, and it is intended to produce preprints of the papers to be despatched to delegates in advance of the Conference.

Any persons interested should write to the Director & Secretary of the Association, Mr R. H. Hamblin, at the address on the Contents page, to receive full details as these become available.

SYNTHETIC RESINS TECHNOLOGIST  
REQUIRED

A major synthetic resins manufacturing company presently producing alkyds require a synthetic resins technologist for a new plant being set up in Karachi, Pakistan for a minimum period of one year. Should have thorough knowledge and practical industrial experience in manufacture of various paint resins, particularly alkyds and phenolics. Consultants also to be considered. Terms very attractive with up to fifty per cent paid abroad. Accommodation, transport etc. provided. Would prefer older person with long industrial experience. Please contact by letter giving all particulars and salary expected to following:

**A. J. JAMIL**  
**45 MEADOWBANK**  
**LONDON N.W.3**  
**TELEPHONE OFFICE: 628-3135**

Chemical Society Symposium

**Pigments—Health & Safety factors**

The Industrial Division of the Chemical Society is organising a one-day symposium on Thursday 19 October 1978 on 'Pigments—Health and safety factors', at the Scientific Society Lecture Theatre, 23 Savile Row, London W1.

CLASSIFIED ADVERTISEMENTS

APPOINTMENTS VACANT



We are the parent company of a young International Group, manufacturing and marketing a successful range of paints and specialist surface coatings.

**WE OFFER:** membership of a young team of executives, each enthusiastically co-operative and crisply efficient in his own sphere.

Modern laboratory and works premises and equipment, Attractive salary, bonuses, company car, pension and life assurance. Four weeks' holiday per annum.

**JOB SATISFACTION AND FREEDOM TO BE EFFECTIVE**

**WE NEED:** a **SENIOR PAINT CHEMIST**  
**CHIEF CHEMIST/TECHNICAL MANAGER**  
**DESIGNATE**

having appropriate academic qualifications and the wide practical experience of all aspects of paint formulation and manufacture to enable the successful candidate to rapidly assimilate the needs of the group and take full control of our technical operations.

**A PERSON WHO CAN GROW WITH US AND THE JOB**

**THE JOB:** offers much scope for originality, imagination, and progressive advancement. May ideally suit able, senior chemist whose promotion is presently blocked.

Write in confidence, stating qualifications, and experience, to: Managing Director.



GLENBURN RD., COLLEGE MILTON, EAST KILBRIDE, GLASGOW G74 5BA

**FURNITURE MATERIALS RESEARCH**



FIRA is the world's leading Research authority and technology centre within furniture manufacture and its associated materials and processes.

A scientist is required to work within the Materials Technology section of Research in a group concerned with sheet materials, finishes and adhesives. The work involves research into finishing materials and application methods, testing and fault finding both in the laboratory and in factories throughout the U.K.

The successful applicant will probably have a degree in chemistry, physics or physical chemistry and have several years' industrial experience.

Promotion prospects and conditions of employment in FIRA are very good.

Please apply in writing to:

**Michael Charity**  
**Head of Research**  
**Furniture Industry**  
**Research**  
**Association**  
**Maxwell Road**  
**Stevenage**  
**Herts SG1 2EW**

**Hull Section**

**Dinner & Dance**

The Hull Section Dinner and Dance will be held on Friday 6 October 1978 at the Willerby Manor Hotel, Willerby, Nr Hull. Tickets price £7.50 inclusive of VAT.

Tickets available from:

**The Hon. Social Secretary,**  
**Hull Section, OCCA,**  
**A. R. Van Spall, Esq,**  
**Jusrite, 5 Middle Garth Drive,**  
**South Cave, Brough HU15 2AY**

**OCCA-31**  
**Exhibition**



Intending exhibitors are reminded that the closing date for returning application forms is

**31 October 1978**

Any organisation which has not yet received an Invitation to Exhibit and wishes to do so should contact the Director & Secretary at the Association's offices

Telephone 01-908 1086  
Telex 922670 (OCCA G)

## APPOINTMENTS VACANT

## PAINTECHNOLOGIST

We are leading manufacturers of synthetic resin emulsions which are essential raw materials for paint, adhesives, paper and textile applications. We sell directly in the UK and Western Europe but in addition have worldwide outlets and licensing arrangements in many countries. We require an experienced Paint Technologist to lead application development and customer service in our research and application team.

The ideal candidate will have experience in paint formulation, knowledge of polymer and/or surface chemistry and well developed leadership qualities. A certain amount of travel in Europe is envisaged and some ability in French/German would be an advantage.

The salary and fringe benefits will reflect the importance of this key position. Promotional prospects are good. Our modern laboratories are situated at Carshalton with easy rail and road access for London and the Southern Home Counties. Generous assistance with relocation expenses will be given where appropriate.

Please apply to Alan Rutter, Company Personnel Manager, giving details of age, qualifications and experience, and how you wish to see your career develop over the next few years. All replies will be treated in the strictest confidence.

Vinyl Products Limited,  
Mill Lane, Carshalton,  
Surrey SM5 2JU.  
(A Unilever Company.)



### Water-thinnable coatings

The Borough Surface Coatings Association of the South Bank Polytechnic is organising a one-day symposium on 'Water-thinnable coatings' to be held on Tuesday 10 October 1978. Those wishing to receive details or application forms should write to:

**P. J. Barnes,**  
Dept. of Chemistry,  
South Bank Polytechnic,  
Borough Road,  
London SE1



AT ANY TIME  
DAY OR NIGHT

TELEX  
YOUR CLASSIFIED  
FOR  
JOCCA

Telex 922670 (OCCA Wembley)

See page xx for details of rates  
for Classified Advertisements.

### RECONDITIONED EQUIPMENT FOR SALE

### Flame-proofed Battery Electric Forklift Trucks!!!

By Conveyancer. 4500lbs capacity. Lifting heights from 9ft to 20ft. Also a full range of conventional Battery Electric Forklift Trucks. Full details and photographs available from:



**Speed Electrics, The Wells Road, Nottingham.**

Tel: 0602-609782

## INDEX TO ADVERTISERS

<b>A</b>		<b>H</b>	
Ashby, Morris, Ltd...	iv	Hardman, E., & Co. Ltd	ii
<b>B</b>		Henkel & Cie GmbH	Insert
Bray, E. P., & Co. Ltd	viii	Highgate & Job Ltd	i
<b>C</b>		<b>I</b>	
Croda Resins Ltd	vi	ICI Ltd—Organics Division	x, xi
Crosfield, Joseph, & Sons Ltd	Insert	<b>M</b>	
<b>D</b>		Madley, Richard, (Printers) Ltd	iii
Dow Chemicals—Methocel	ix	Mettler Instruments AG	xv
<b>E</b>		<b>Q</b>	
ECC International Ltd	v	Q-Panel Co.	ii
<b>F</b>		<b>S</b>	
Färg och Lack	iii	Sachtleben	xii
Federation of Societies for Coatings Technology	Cover	Sheen Instruments (Sales) Ltd	xix
<b>G</b>		Shell International Co.	xvi, xvii
Glen Creston Ltd	Cover	Sub-Tropical Testing Service Inc.	i



# 1978 Annual Meeting and Paint Industries' Show

## COATINGS: The Search for Opportunities

- Three days of technical sessions ● Exhibits of 126 supplier companies, whose top technical people will be on hand to discuss latest developments ● Opportunity for one-on-one interchange with Executives, Purchasing Agents, Chemists, Engineers, and Research, Development, and Production Personnel of the Coatings Industry ● All under one roof.

- Plan NOW to attend this Major Coatings Event ● Save time and money by registering in advance ● Copies of registration and housing forms available from FSCT headquarters.



**FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY**  
1315 Walnut Street • Philadelphia, Pa. 19107 • 215/545-1506

OIL & COLOUR



CHEMISTS'

ASSOCIATION



TECHNICAL EXHIBITION

3-6 APRIL 1979

The motif for OCCA-31, designed by Robert Hamblin, emphasises the unique aspect of the OCCA Exhibitions, which annually provide an international focal point for the surface coatings industries. In 1978, exhibitors were drawn from sixteen countries and visitors from over fifty countries.

COMPLETE AND RETURN THIS COUPON FOR A COPY OF THE INVITATION TO EXHIBIT

To: Director & Secretary, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF ENGLAND  
Telephone 01-908 1086 Telex 922670 (OCCA WEMBLEY)

We are interested in exhibiting at OCCA-31 (3-6 April 1979, Alexandra Palace, London). Please send us a copy of the Invitation to Exhibit.

BLOCK LETTERS PLEASE

3 APR 1979