OCCA GOLF TOURNAMENTS

**London Section** 

Wednesday 8 July 1981

For further details

see page xiii

**Northern Sections** 

Thursday 25 June 1981

For further details

see page vi



# J O C C A

# OURNAL<sup>®</sup>OF THE IL & OLOUR HEMISTS' SSOCIATION

\*\*\* WINNER OF THE 1980 ABC REED INTERNATIONAL AWARD

Organotins in wood preservation

C. J. Evans and R. Hill

Recent formulation developments in chlorinated rubber paints *R. G. Humphries* 

Further investigation of the photo-induced oxidation of normal primary alcohols by anatase titanium dioxide *M. A. Malati and N. J. Seager* 

Estimation of shellac

N. Prasad and B. B. Khanna

Priory House, 967 Harrow Road, Wembley, Middlesex, HAO 2SF England

## **Q~Panels** ve a rri

The Q-Panel Company of Cleveland, U.S.A., probably the worlds largest manufacturer of steel and aluminium panels for coating evaluation have now opened a European Branch Office. The office is a marketing, distribution and technical advisory centre for the well established range of Q-Panel products.

Q-Panels-coating test panels are available in a full range of sizes and surface finishes at a remarkably low price.

Q.U.V.-Accelerated Weathering Tester simulates the damaging effects of sunlight and moisture. Advantages of the design include faster tests, closer control, and reduced operating costs.



Rounded corners and deburred edges.



Price Panels are degreased per 100 6" × 4 Dull Matt finish prior to packing. steel 0.032 thick £13.50

and VAI

PANE

The Q-Panel Company, 102 Taylorson Street, Ordsall. Salford M5 3HA. Telephone: 061-872 1152

Reader Enquiry Service No. 111



### **Quality Control Procedures** When Blast Cleaning Steel

This Special Publication is intended to bring readers up to date with present international thinking on the best quality control procedures to use for measuring the profile and cleanliness of blast-cleaned steelwork

The procedures described apply not only to the various rust grades of unprotected steel but also to the blast cleaning of previously protected steel which has become rusty.

In surveying methods of assessing profile, panels representative of a wide range of blast cleaning methods in a number of countries have been examined and their profile characteristics established. The statistical analysis of the results presented enables definition of the best practical approach to profile assessment. It is hoped that the methods proposed will soon be embodied in a new International Standard.

Candidate chemical and physical methods for determining levels of cleanliness are reviewed. These are assessed as practical test methods to supplement visual determinations.

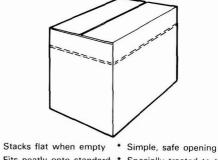
Price: £25 (Paint B A Members - £21)

> Available from Mrs Caroline Veitch Publications Co-ordinato Information Department Paint Research Associative Waldegrave Road Teddington, Middlesex TW11 8LD

Reader Enquiry Service No. 109

## СНЕМРАК

The MODERN pack for powder and paste chemicals, and it's RECTANGULAR so there's no more wasted space.



- Fits neatly onto standard \* pallets
- - Specially treated to take toxic chemicals
  - \* Lower storage, handling and shipping costs

For further details contact: HILLWOOD Ltd. Friars House. 39.41 New Broad Street, London EC2M phone 01-628-5988 telex 377885

Kender En juiry Service No. 103



# A new brightness from ECC International

PoleStar 200P is one of the new PoleStar range of calcined clays from ECC International, developed as an extension to our existing range.

Special processing means PoleStar 200P (the P is for Paint) has even more of the brightness you've been looking for in an extender. And you'll need less TiO<sub>2</sub>. PoleStar 200P may be just the

bright idea you've been looking for. Why not ask us about its cost effectiveness? The PoleStar range – a new direction in calcined clay



technology.

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

#### OIL & COLOUR CHEMISTS' ASSOCIATION-PUBLICATIONS



The Introduction to Paint Technology, of which 20,000 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. The text has been thoroughly revised and updated to incorporate recent advances in technology of the surface coatings industries.

Price: £5.00 (US \$12.00)

### 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 (US \$7.00)** 

### **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 (US \$12.00)

**1975 Scarborough** Performance of surface coatings -does reality match theory? Seventeen papers presented. **Price: £5.00 (US \$12.00)** 

1973 Eastbourne *Towards 2000.* Sixteen papers presented. Price: £5.00 (US \$12.00)



Ultraviolet polymerisation and the surface coatings industries The Association has published two volumes on this

subject comprising 23 papers presented at Symposia, forming an authoritative work of reference for this rapidly developing technology. Special offer: £10.00 (US \$24.00) for both volumes purchased together.



Monograph No. 1. MARINE FINISHES. Now available Price £2.00 (US\$5.00) ORDER FORM

To: **Oil & Colour Chemists' Association**, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, England. I enclose remittance of £ (US \$).....to cover the cost.

Name: \_\_\_\_

Please send me copies of the books as listed below:

Address to which books should be sent:

Prices include postage and packing (surface mail).

# The new suspender

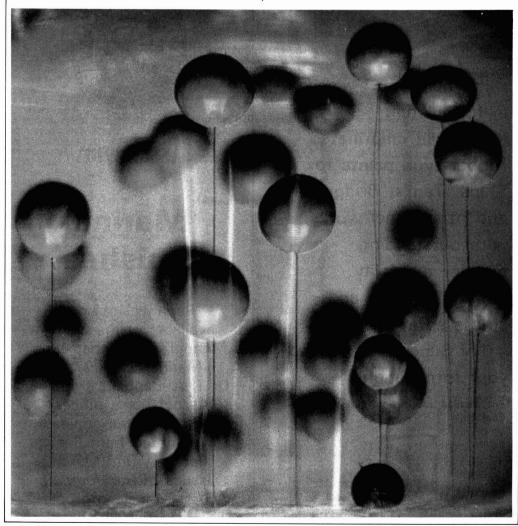
## M-P-A\* 2000 X

is a new rheological additive for anti-settling agent industrial finishes. It keeps pigment particles in suspension and minimizes settling. M-P-A 2000 X has two outstanding advantages: it is highly efficient and it pours. For further information please contact

#### NL CHEMICALS (UK) LIMITED

St. Ann's House Wilmslow, Cheshire SK9 1HG Tel: 0625/529511 Telex 669055

\*Trademark of NL Industries, Inc.







Reader Enquiry Service No. 107



Try Superchlon for your formulations.

For detailed information, please contact:



Sanyo-Kokusaku Pulp Co.,Ltd. CHEMICALS SALES DEPT.

1-4-5 Marunouchi, Chiyoda-ku, Tokyo, Japan Telex: J24279 SKPULP Cable: SANKOKUPA TOKYO

Reader Enquiry Service No. 112

## **OIL & COLOUR CHEMISTS'**



## ASSOCIATION

## Marine Finishes

Reprints are now available of the OCCA Monograph number 1 on Marine Finishes by Dr T. A. Banfield from the Association's offices. These bound copies reprinted from the February and March issues of the *Journal* cost £2 including post and packaging.

## JOURNAL of the OIL AND COLOUR CHEMISTS' ASSOCIATION

Hon. Editor: D. S. Newton, AMCT, CGIA, FICorrT, FIMF, FTSC	Contents	Vol. 64 No. 6	June 1981
Publications Committee:			
J. Ambury T. A. Banfield, PhD, DIC, ARCS, Flnst.CorT, FTSC H. I. Bosman, BComm, FTSC J. Bourne, FTSC	Transactions and Con	nmunications	
J. Bourney, FISC T. Entwistle, CChem, FRSC, FTSC A. W. Fell, BSc, AMCT, ATSC C. N. Finlay, ATSC S. R. Finn, BSc, CChem, FRSC, FTSC H. R. Hamburg, PhD, FTSC T. Harbottle	Organotins in wood		215 ans and R. Hill
<ul> <li>T. J. S. Henning</li> <li>A. MacDonald, ATSC</li> <li>W. MacDonald</li> <li>D. V. Maltman</li> <li>P. McCrudden</li> <li>D. J. Morris</li> <li>B. E. Mvatt</li> </ul>		developments in chlorinate	
<ul> <li>A. J. Newbould, BSc, CChem, MRSC</li> <li>F. D. Robinson, BSc, ATSC</li> <li>T. W. Slinn, BSc, FTSC</li> <li>F. M. Smith, BSc, PhD, CChem, FRSC, CCol, FSDC, MIOP, FTSC</li> <li>J. R. Taylor, BSc, CChem, FRSC, FTSC</li> <li>E. G. Warman, FDISA</li> </ul>		n of the photo-induced oxic Icohols by anatase titanium 	231
F. B. Windsor, ATSC Editorial correspondence should be addressed to the Hon. Editor, <i>JOCCA</i> , Oil and Colour Chemists' Association at the address below.	Estimation of shella	<b>c</b>	234 B. B. Khanna
General correspondence should be addressed to:	Letters		237
R. H. Hamblin, MA, FCIS, Director and Secretary, Oil and Colour Chemists' Association at the address below.	Reviews		238
Tel: 01-908 1086 Telex 922670 (OCCA G) Telegrams: OCCA Wembley Telex	OCCA Meetings .		238
Assistant Editor: D. N. Buddles, BSc	News		241
Annual subscription to non-members: £40.00 (\$100), post free by surface mail, payable in advance.			241
Single copies £4.00 (\$10), post free by surface mail, payable in advance.	OCCA News		246
© Copyright 1981	New members .		248
OIL AND COLOU Priory House 967 Harrow	R CHEMIS	STS'ASSO(	

## 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

#### -4. 1.1.2525

### The 1981 Northern Sections' Golf Tournament organised by the Manchester, West Riding, Hull, Newcastle and Scottish Sections

#### **Final Notice**

- **Competitions:** Tony McWilliam Trophy open to OCCA members only. Additional competitions will be arranged.
- Course: Pannal Golf Club, Pannal, Near Harrogate, Yorkshire. Tel: 0423 871641. Situated on the Leeds to Harrogate Road – A61.

Date: Thursday 25 June 1981.

**Starting Time:** Tee reserved from 1.30 p.m. onwards – 3 player grouping at 6 minute intervals.

- **Type:** Singles Stableford. Handicap allowance 7/8. Maximum allowance 18 strokes. Competitors will play off their lowest club handicap. Any competitor without a current handicap will be allocated one, prior to starting, by a sub-committee.
- **Cost:** £11.50 per head (cheque made out to OCCA Manchester Section) covering the cost of green fees, evening meal, gratuities and VAT, but not sandwiches at lunch-time.
- **Catering:** An evening meal has been arranged, presentation of the prizes will also take place during the evening.

Sandwiches will be available, at extra cost, between 12 noon and 2.00 p.m.

Eligibility: OCCA members and their guests. Maximum numbers of entrants will be 60. Preference will be given to OCCA members. If it proves necessary to form a waiting list only those on the list will be notified. Notification of withdrawal from the competition to be made to the undersigned as soon as possible.

Prizes: Offers of prizes to add incentive to the competition will be greatly appreciated.

**Application:** Members wishing to take part are requested to complete and return the attached slip plus £11.50 remittance not later than 11 June 1981.

### 1981 Northern Section's Golf Tournament

To: F. B. Windsor, ATSC,	I wish to enter for the Tony McWilliam Trophy				
England, Hughes, Bell & Co. Ltd, Valley Works, Monton Road, Eccles, Manchester M30 9HJ. Tel: 061-789 5191.	I will require sandwiches at lunch-time				
	I will require an evening meal(s) (Enter No. required)				
OCCA Member	Guest(s)				
Name					
Address					
*****	•••••••••••••••••••••••••••••••••••••••				
Tel					
Handicap					
Signed					

#### **Transactions and Communications**-

## Organotins in wood preservation

#### By C. J. Evans and R. Hill

International Tin Research Institute, Fraser Road, Perivale, Middlesex, England

#### Summary

The current position of the use of organotin compounds as fungicides for wood, whether painted or not, is reviewed.

At present bis(tributyltin)oxide is the most widely used substance; the maximum activity occurs when the alkyl chains attached to the tin atom contain a total of nine to twelve carbon atoms. The composition of the other group or atom attached to the tin atom has a minor effect on the activity. When this group

#### Keywords

Types and classes of coatings and allied products

wood preservative

Types and classes of structures or surfaces to be coated

timber wood

Processes and methods primarily associated with surface preparation before coating

pretreatment

is of the type  $-SO_3$ .R it becomes possible to confer a sufficient degree of water solubility for most biocidal applications.

The mechanism of the breakdown of wood by fungi and some insects is reviewed and possible ways in which organotin compounds may prevent the breakdown are discussed.

Some methods of impregnation and treatment of timber with fungicide are described.

Raw materials for coatings biologically active agents

> fungicide fungistat microbiological agent organo tin tributyl tin oxide

#### Les composés organiques d'étain dans le domaine de la préservation de bois

#### Résumé

On passe en revue la situation actuelle à l'égard de l'emploi des composés organiques d'étain en tant que fongicides pour être appliqués au bois soit peint ou non.

A présent la substance la plus utilisée est bis(stanntributyle) oxyde. L'activité maximale se produit où les chaînes alkyles attachées à l'atome d'étain comprennent en totale neuf à douze atomes de carbone. La nature de l'autre atome ou groupement attachée à l'atome d'étain n'exerce qu'une influence peu importante sur l'activité. Lorsque ce groupement-ci est du type -SO<sub>1</sub>.R. il est possible d'accorder au composé un degré de

#### Die Organozinnverbindungen in Holzschutzmitteln

#### Zusammenfassung

Ein Überlick über die gegenwärtige Lage wird hinsichtlich der Anwendung von Organozinnverbingungen als Pilzgifte für lackiertes sowie nacktes Holz gegeben.

Die bis(Tributylzinn)oxyd steht gegenwärtig als die angewendetste Substanz. Die höchste Aktivität zeigt sich wenn die mit dem Zinnztome verbundenen Alkylketten ins Gesamt neun bis zwölf Kohlenstoffatome enthalten. Die Zusammensetzung der anderen Gruppe oder Atome, die mit dem Zinnatome verbunden ist, wirkt nur einen geringen Einfluss auf die Aktivität. Wenn diese Gruppe der  $-SO_{\rm V}R$  Typ ist, ist es

solubilité à l'eau qui est suffisante pour la plupart des besoins biocides.

On considère les mécanismes de pourriture de bois provoquée par les plantes mycélliennes et par certains insectes, et l'on discute les moyens éventuels par lesquels les composés organiques d'étain pourraient empêcher cette pourriture.

On décrit quelques méthodes pour effectuer l'impregnation et le traitement de bois par fongicide.

möglich eine Wasserlöslichkeit darzustellen, die für die meistenen Biozidanwendungen genügend ist.

Ein Überblick über den Holzzusammenbruchmechanismus, der von Pilzen und Insekten verursacht wird, wird gegeben und es wird ebenfalls diskutiert wie möglicherweise mittels Organozinnverbindungen der Zusammenbruch verhindert werden könnte.

Einige Methoden zur Imprägnierung und Behandlung des Holzes mit Pilzgift werden beschrieben.

#### Introduction

Wood has many advantages as a material of construction and even in this period of high technology it is still widely used. Wood is easily worked and shaped, it has a high strength-to-weight ratio and can be decorated by painting or varnishing; in thick sections it is surprisingly fire-proof. Perhaps even more significant today is the fact that it is a renewable resource, since the source of all timber, the tree, can be planted and harvested. Yet this last factor is connected with its one serious limitation, the fact that as a natural material it is subject to biodeterioration. Under certain conditions, wood may be attacked by fungi which undermine its structure as well as damaging its appearance; wood-boring insects can have a similar deleterious effect on its strength. The ravages which may be caused in extreme cases are evident in many historic old buildings (and in some of more recent origin). Modern building methods tend to increase the risk of attack; thinner structural sections are being specified in order to make existing resources meet increasing demand and trees are being felled before reaching full maturity (which means that the proportion of less-resistant sapwood is higher than in the past). The common use of higher heating levels in dwellings, together with the adoption of paint finishes which prevent the evaporation of dampness from external joinery timber, also make the problem of timber decay more pressing.

Fortunately timber treatment techniques have been developed which can adequately cope with these problems. Specialist companies are able to repair old wooden structures which have been attacked and can prevent further deterioration. Yet this can be costly and timeconsuming and on the principle that "prevention is better than cure", most timbers for modern buildings, particularly joinery and roofing beams, are pre-treated with a suitable preservative to ensure long-term built-in protection. That this is possible is due largely to the discovery of potent biocidal agents which are organic solvent-based and which can be applied conveniently to timber components, without damaging their appearance or other properties. Prominent amongst these biocidal agents are the organotin compounds and particularly tributyltin compounds. The use of these chemicals in wood preservation is described in this paper and theories regarding their mode of action are reviewed. The International Tin Research Institute has a programme of research in this field and the findings are included wherever relevant.

#### Organotins in wood preservation

#### Refs, 1-8

The biological activity of organotin compounds varies considerably according to the number of organic groups attached to tin, with the highest activity being shown by compounds having three Sn–C bonds. In triorganotin compounds, R<sub>3</sub>SnX, the nature of the anionic group, X, does not significantly influence the biocidal activity, which depends largely, in trialkyltin compounds, on the number of carbon atoms present in the three alkyl chains. Maximum activity is associated with a total of 9-12 carbon atoms, regardless of the nature of the individual alkyl groups. Tributyltin compounds are more easily prepared industrially than are their unsymmetrical trialkyltin analogues and they also exhibit the widest separation between mammalian toxicity and biocidal activity against fungi. For these reasons, most organotin wood preservatives have been based on tributyltin compounds. By far the most widely used organotin preservative is bis(tributyltin)oxide (TBTO) and its use has grown steadily since its introduction in the USA in 1959<sup>1</sup>. Today over sixty commercial preservatives based on this compound are available in the UK alone<sup>2</sup>.

Bis(tributyltin)oxide is a colourless liquid with a kinematic viscosity of 4.8 centistokes at 25°C, a specific gravity of 1.17 at 20°C, a refractive index at 20°C of 1.488, and a boiling point (at 2 mm mercury) of 180°C. The organotin is normally used in an organic solvent such as kerosene, at concentrations between 1 and 3 per cent depending on the type of wood and the intended end use. TBTO\* does not discolour wood which has been impregnated with the chemical and the wood can be painted or glued in a normal fashion once dry; the flammability of the wood is not increased by the presence of TBTO once the solvent has evaporated. The compound has a characteristic odour, but at the low concentrations at which it is employed in wood preservation, no odour is noticeable. The acute oral toxicity (LD 50) of TBTO for rats is approximately 200 mg/kg. Tributyltin oxide is active against a wide range of fungi and gram positive bacteria; it also has insecticidal properties3, which in commercial formulations are often reinforced by the addition of a contact insecticide, the two compounds often having a mutual synergistic effect as will be discussed later. A British Standard Specification for the material exists: BS 4630 : 1970, "Tributyltin oxide for use in paint, paper, timber and textiles as a preservative against microbiological growth". The organotin is used in the pre-treatment of building timbers as well as in remedial treatments.

The use of tributyltin compounds in wood preservation has been reviewed by Hof<sup>4</sup> and by Richardson<sup>5</sup> and more recently by Smith *et al*<sup>6</sup>. From these reviews it is evident that there have not been many reported attempts to screen organotin compounds as potential wood preservatives using wood-block tests. In view of this, a series of tributyltin compounds, Bu<sub>3</sub>SnX, has been synthesised at the International Tin Research Institute and their fungicidal activity assessed against *Coniophora puteana* (cerebella) and *Coriolus (Polystictus) versicolor* on *Pinus* sylvestris (Scots pine) blocks on agar. Table 1 contains initial results from this test programme which was based on a specially developed wood-block agar test<sup>7</sup>.

The test method was similar to that outlined in British Standard Specification 838:1961, in that replicate blocks of Scots pine sapwood were treated with a series of successive dilutions of preservative solution, dried, sterilised and exposed to pure cultures of two wood-destroying Basidiomycete fungi, *Coniophora puteana* and *Coriolus versicolor* growing on malt agar. Weight losses occurring during incubation were measured and the toxic limits determined. The use of small test blocks ( $30 \times 10 \times 5$  mm) allows a shorter incubation period (6 weeks) than that specified in BS 838, and small culture vessels (9 cm Petri dishes) could be used with simple incubation facilities.

One aim of the series of tests was to compare the toxicity of particular tributyltin compounds with that of TBTO. Thus, the solution concentrations of preservative were adjusted to give tributyltin loadings in wood

\*TBTO is used throughout this paper as an abbreviation for bis(tributyltin)oxide, not as a trade name

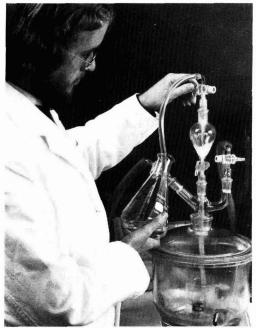


Figure 1. A number of organotin compounds have been prepared at the International Tin Research Institute for testing as wood preservatives. Photograph courtesy: ITRI

corresponding to those obtained with TBTO at, above and below, the published toxic level of TBTO. For comparative purposes, TBTO was also included in the test series.

The general similarity in the toxic limits found for the compounds suggests that their efficacy is not influenced by the nature of the X group. It is interesting to note that tris(tributyltin)phosphate<sup>2</sup> and tributyltin naphthenate<sup>8</sup> have recently found limited commercial use as wood preservatives.

#### Mechanisms of fungal attack

#### Refs, 9-13

In order to understand the mechanisms by which wood is attacked by fungi and the ways in which preservatives prevent decay, it is necessary to consider briefly the structural features of wood. These have been described in the comprehensive book on "Wood Preservation" by Richardson<sup>9</sup>. The source of all timber is the tree; this consists of roots, a trunk and the crown of leaves and branches. The trunk is the portion involved in production of structural timbers. A central pith is surrounded by a series of concentric cones; wood tissue around the pith is termed heartwood and consists of dead cells. Then come the living cells of the sapwood or xylem, which in turn is covered by a thin layer of phloem cells and protective bark. The interface between the xylem and the phloem cells is termed the cambium and this is made up of actively dividing cells which split off to join the xylem or the phloem. Growth of the xylem deposits tend to be seasonal and varies from a wide band of large but thin-walled cells (early growth) to much smaller thick-walled cells (summer or autumn growth). The annual rings, visible in cross section when a tree is felled, represent the transition between these types of cells. The xylem or sapwood is the tissue that conducts water and dissolved salts from the roots to the crown of the tree. Phloem conducts sugars from the crown to the various growing cells throughout the structure of the tree. When a xylem cell is first formed, it consists of a thin wall constituted by sugars which have polymerized into cellulose. Sugars from the phloem continue to be supplied to the xylem cells so that successive secondary layers of cellulose are formed within the original primary wall. Once the cell structure is complete, much slower processes of lignification occur consisting of a progressive deposition of lignin, initially within the middle lamella (amorphous undifferentiated region between cells) and then within the cell walls. This serves to stiffen and strengthen the cells. A schematic interpretation of the cell structure<sup>10</sup> is shown in Figure 2.

The principal difference between sapwood and heartwood is the large amount of waste matter (arising from living processes within the tree) deposited in the latter. These reduce porosity and are often toxic; heartwood is therefore more resistant to insect and fungal attack and to swelling and shrinkage with changes in moisture content. The relative amounts of heartwood and sapwood are regulated by dynamic living processes in the

	Table 1	
Some	tributyltin compounds tes.	ed for antifungal
	activity at the Inst	itute

Compound	Fungus	Toxic limits (loading in wood blocks kg m <sup>-3</sup> )
ТВТО	C.p. C.v.	0.19-0.70 0.20-0.69
(Bu <sub>3</sub> SnO) <sub>3</sub> B	C.p. C.v.	0.38-0.96 0.19-0.37
(Bu <sub>3</sub> SnO) <sub>2</sub> CO	C.p. C.v.	0.20-0.38 0.20-0.38
(Bu <sub>3</sub> SnO) <sub>3</sub> glucose	C.p. C.v.	0.46-1.14 0.47-1.17
(Bu <sub>3</sub> SnO) <sub>4</sub> cellobiose	C.p. C.v.	0.48-1.14 0.45-1.17
(Bu <sub>3</sub> SnO) <sub>7</sub> -cyclodextrin	C.p. C.v.	0.32-0.62 0.61-1.60
Bu <sub>3</sub> SnONO <sub>2</sub>	C.p. C.v.	0.48-1.13 0.45-1.16
(Bu <sub>3</sub> SnO) <sub>3</sub> PO	C.p. C.v.	0.38-0.96 0.39-0.99
Bu <sub>3</sub> SnOSO <sub>2</sub> .Et (tributyltin ethanesulfonate)	C.p. C.v. C.p.† C.v.†	0.49-1.21 0.24-0.50 0.58-1.18 0.58-1.17
Bu <sub>3</sub> SnNCS	C.p. C.v.	0.23-0.44 0.44-1.14
Bu <sub>3</sub> SnSCH <sub>2</sub> .CO.O(i-C <sub>8</sub> H <sub>17</sub> )	C.p. C.v.	0.63-1.64 0.64-1.54
$(Bu_3Sn)_2S$	C.p. C.v.	0.40-1.03 0.39-1.00
Bu <sub>3</sub> SnCl	C.p. C.v. C.p.§ C.v.§	0.38-0.97 0.39-0.98 0.16-0.31 0.31-0.61

C.p. = Coniophora puteana \*Mean values from several tests \*Applied in water \$Applied in acetone

In all other cases the solvent was petroleum ether.

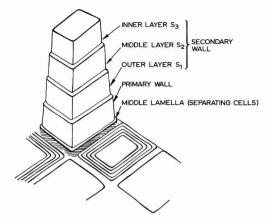


Figure 2. Structure of a wood cell. Cells are 1-5 mm in length and about 95 per cent are aligned along axis of tree trunk. Cell walls are made up of: 45-50 per cent (wt.) microfibrils of a crystalline cellulose polymer containing 5000 glucose units; 20-25 per cent (wt.) semi-crystalline non-cellulosic polysaccharides; and lignin amorphous 3 dimensional molecules of phenol propane units

tree, cells dying off as new ones are produced. The practice of cutting down trees before they have reached full maturity means that there is a greater proportion of less resistant sapwood in the timber so produced.

It should be emphasised that fungal attack of wood only occurs when the wood has a high moisture content and has access to air. Fungi attack wood by the action of enzymes which bring about decomposition of the cell wall components. According to some theories11.12, bacteria are initially responsible for the breakdown of the pits in the sapwood, opening up the wood structure and making it more permeable to liquids and gases so that fungal growth is possible. Primary moulds then enter sapwood cells through these initial pathways. The polymeric cell wall constituents are hydrolysed by the enzymes and oxidised into low molecular weight soluble or volatile products. These primary products of decay are then partially absorbed by the fungus and serve as a source of nourishment for it. The first stage consists of invasion of the cellular passages in the wood by long, thread-like tendrils known as hyphae. Natural pits in the wood allow the hyphae to progress from the initial pathways into adjacent tissues. There is an initial period of passive vegetative growth when the wood substrate is rapidly and extensively colonised. The hyphae then grow preferentially through the largest available voids in the substrate and into the nutrient-rich tissues containing simple sugars. In the early stages the hyphae grow from cell to cell through natural pit openings rather than by boring through lignified cell walls. Extra-cellular secretions actively degrade the components of the cell wall and these lysis patterns are determined by the type of invading fungus and by the nature of the secretions which degrade the cell wall. Physical and chemical differences in the cell wall structure of particular types of wood also modify these lysis patterns<sup>13</sup>. These phenomena are manifested in the types of behaviour observed in the different types of wood rot.

The wood-rotting fungi can conveniently be divided broadly into three groups, brown rot, white rot and soft rot fungi. Brown rots only attack the cellulose in the wood and the predominant enzymic action is hydrolysis of the polysaccharides. The well-known dry rots and wet rots are typical examples of brown rot; of all fungal decay found in buildings and structures, about 95 per cent can be attributed to one or other of these rots. Dry rot, *Merulius* lacrymans, is the most widely known cause of damage in buildings. Dry rot spores will germinate only when the atmospheric relative humidity is suitable, generally where accidental wetting has allowed wood to become very wet. Subsequent drying may permit the relative humidity to reach the optimum level for spores to germinate; this consists of the development of hyphae which penetrate into the wood and which spread, so that the affected area is covered with a soft, white growth, like cotton wool. Under suitable conditions, a dense skin or mycelium may form on the surface of the wood. The hyphae will spread across and through plaster, brickwork, masonry and concrete. As attack continues the cellulose is destroyed, giving the wood the characteristic colour of a brown rot. accompanied by pronounced longitudinal and cross-grain cracking which results in a cuboid formation in the wood. When the fungus is exposed to light, fruiting bodies are also produced. Wet rot, Coniophora puteana depends for its existence on continual dampness or running water to keep the wood damp. It is thus commonly found in roofing timbers and in fence posts. The early growth has a fluffy, whitish appearance, soon developing into a stringy shape of fine strands which may be brown or blackish in colour. The wood may also darken in colour and crack lengthwise; fruiting bodies are not often found in practice.

White rot fungi attack both the lignin and the cellulose in the wood, oxidising enzymes attacking the lignin. *Coriolus versicolor* is the commonest cause of white rot in hardwoods, especially in ground contact as in pit props. The sporophore is rarely seen, but consists of a thin bracket up to 75 mm across, grey and brown on top, with concentric hairy zones and a cream pore surface under-

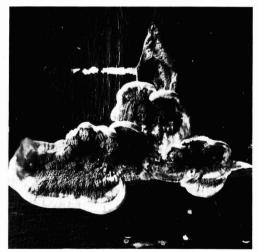


Figure 3. Fruiting bodies of the dry rot fungus Merulius lachrymans

neath from which the spores are released. Decayed wood appears to be lighter and much weaker than sound wood.

Soft rot fungi may attack wood which is waterlogged, and are particularly prevalent on the wooden fillings of water-cooling towers. The fungi are primarily cellulose destroyers and attack is usually superficial, so that, except in thin sections of timber, there is less weakening action. Softwoods as a class are more resistant to soft rots than are hardwoods, possibly because of the higher degree of lignification of the secondary cell wall in softwoods, which protects the cellulose from attack.

Recent work<sup>11</sup> on the mechanisms by which fungi decay wood has been concerned with attempts to understand how the decay patterns of brown, white and soft rot fungi occur in terms of their respective enzyme activity. Evidence has been produced to demonstrate that the enzymes of the soft and white rot fungi are restricted in their activity to regions of close proximity to the hyphae, whereas those of the brown rot fungi appear to be acting at a much greater distance. Thus it has been postulated that the enzymes of soft and white rots are linked to the hyphae, whereas those of the brown rots are not.

#### Mode of action of organotin preservatives

#### Refs, 7, 11, 13-22

The mechanism by which organotin compounds protect wood against fungal attack is still not completely understood. Certainly, the anti-fungal action of TBTO as determined in vitro differs from the actual behaviour exhibited in wood samples against the same fungal species. Factors such as the type of wood, the depth of penetration of preservative into the wood and the long-term stability of the toxicant in situ all play a part. It has been observed that tributyltin compounds are most effective as wood preservatives against brown rot fungi, which destroy cellulose, but rather less effective against white rots, which attack both cellulose and lignin, for which higher loadings are required to confer protection. It has also been observed that brown rot hyphae can spread across and penetrate, wood treated at retentions close to the toxic limit, with the result that regions with an inadequate loading are attacked. Richardson<sup>14</sup> has suggested that the preservative acts by protecting active sites on wood cellulose, rather than by a direct biocidal action on the fungus. This would further imply that the organotin is bound to these active sites on the cellulose chain, in the light of the hypothesis that resistance to brown rots is ensured when two tributyltin groups are present (statistically) for each cellulose chain. Richardson postulated that the organotin condensed onto the hydroxyl groups at the terminal 1 and 4 positions.

However, <sup>119</sup>Sn Mössbauer spectroscopic studies at the Institute<sup>15</sup>, using Scots pine samples, have shown that the organotin compound present in treated wood is bis(tributyltin)carbonate,  $(Bu_3Sn)_2CO_3$ . It was proposed that bis(tributyltin)oxide reacts *in situ* with trapped carbon dioxide, to form the less volatile organotin carbonate, which is a self-associated polymeric species containing penta-co-ordinate tin atoms. Hydrogen bonding between this carbonate and the wood cellulose remains a possibility, but this would not be expected to involve only the terminal 1 and 4 hydroxyl groups. Wood-block agar tests have indicated that bis(tributyltin)carbonate has a very similar activity to the oxide against the brown rot fungus *Coniophora puteana*<sup>7</sup>.

In addition, detailed electron-microscopy studies by Bravery et al.13 provided little evidence to support Richardson's theory that TBTO acts extra-cellularly by blocking the substrate against enzyme activity. These studies demonstrated a possible mechanism for the protective action of TBTO in beech wood. Examination showed that the preservative was distributed uniformly in the wood vessels, but more irregularly in the adjacent fibres. Coriolus versicolor was able to grow into the vessels and fibres, although the initial rate of penetration was retarded, and the fungi were able to produce extra-cellular secretions despite the presence of preservative. Erosion of the preservative deposit was observed, as well as lysis of the underlying cell walls and denaturing of the hyphae. The indications were that solubilisation of the preservative is probably necessary before the toxic components could be released and then absorbed by the hyphae to kill them. Thus, the primary mode of toxic action of tributyltins against fungi appears to be intra-cellular in nature<sup>16</sup>.

In mammals, tributyltin compounds have been shown to be strong inhibitors of oxidative phosphorylation in mitochondria<sup>17</sup> and it has been proposed that the same mechanism is operative in fungi<sup>18</sup>. It has recently been observed that the tributyltin moiety binds to amino acids in certain snail proteins, in addition, studies at the International Tin Research Institute and elsewhere have indicated that HS-groups are involved. The hypothesis that, in the simple Bu<sub>3</sub>SnX compounds, exchange of the X groups at the active protein sites may proceed with relative ease, provides an explanation of the apparent invariance in fungi toxicity with the nature of the group X<sup>19</sup>.

Dickinson and Levy11 have looked at mechanisms of decay and its prevention. One possibility is that the presence of a wood preservative delays the colonisation of both softwoods and hardwoods by groups of microorganisms; this colonisation may be a pre-requisite for fungal attack. Bravery<sup>20</sup> has shown that when tributyltin oxide is incorporated in an organic solvent which induces swelling, the preservative is deposited not only in the cell interior but also within the thickness of the S2 cell wall layer; greater uniformity of distribution between the different wood elements is also achieved. Toxicity testing indicated that Coriolus versicolor (white rot) was inhibited by lower levels of TBTO than when a non-swelling solvent system was used. The improvement in toxic effect could thus be due to the greater resistance of TBTO deposits to enzymatic removal when they are "keyed" into the S<sub>3</sub>/S<sub>2</sub> wall region, than when they are only deposited superficially<sup>16</sup>. In addition, if active protein sites in the fungus involved free thiol groups, as discussed earlier, then TBTO may combine more readily with these in an aqueous medium than in an organic solvent and this has been observed for compounds containing thiol functions.

Workers at the Princes Risborough Laboratories of the Building Research Establishment have reported evidence of degradation of tributyltin to dibutyltin *in situ* in treated wood<sup>21</sup>. This would imply a decrease in protective action since dibutyltin compounds are generally less biologically active than the corresponding tri-organotin. However, a decrease in protective efficiency with time has not been found over 20 years commercial use of these compounds<sup>14</sup>; tests on the degradation have only been conducted on small, unpainted laboratory samples. It is interesting to note that if the organotin merely confers protection by binding to reactive sites on cellulose, then this would not be adversely influenced by some breakdown.

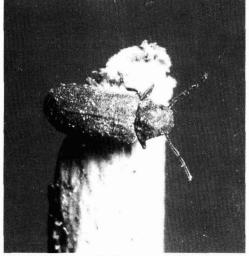


Figure 4. The common furniture beetle, Anobium punctatum. Photograph courtesy: Wykamol Ltd, Winchester

Also of some relevance is the fact that evidence has recently been found for biocidal activity in a dibutyltin compound. In a dental application, dibutyltin dilaurate has been found to inhibit the growth of *Candida albans* on agar<sup>22</sup>.

#### Protection against insect attack

#### Refs. 3, 23, 24

Timber can serve as a food for a few specialised species of insect which are able to bore through it, extract the very small proportion of protein present and either digest cellulose or utilise starchy cell contents as an energy source. Attack by insects is less dependent on moisture in the timber than is fungal attack, although very dry wood is less likely to be attacked.

The most widespread timber attacking pest in Britain is the Common Furniture beetle, Anobium punctatum. This will attack the sapwood of most softwoods and hardwoods, as well as the heartwood of some temperate hardwood species such as birch and beech. Eggs are laid, usually in the summer months, in cracks and crevices in the wooden surface. The larvae hatch out by breaking through the base of the egg and boring immediately into the adjacent wood. The insect usually remains in the larval stage for almost a year before forming a chamber just below the surface in which the full grown larva pupates into an adult beetle. The adult bores to the surface and escapes via a circular flight hole about 1.5 mm in diameter. Damage is caused entirely by the larvae boring through the wood. Prior fungal attack will convert the wood into a form more readily assimilable by the insect.

The Death Watch beetle, *Xestobium rufovillosum* is entirely dependent on prior microbiological attack for its ability to enter the wood. Indeed, wood attacked by this beetle is often brownish in colour, possibly indicating prolonged incipient fungal attack; it particularly inhabits old hardwood timbers such as oak, which have been subject to fungal decay. The larvae hatch after 2-8 weeks and explore the wood before starting to bore down into it. The adult beetle emerges leaving a flight hole about 3 mm in diameter.

The third species of wood boring insect of major significance in buildings is the House Longhorn beetle, *Hylotrupes bajulus*. The larvae feed voraciously on the sapwood of structural softwoods, causing severe destruction and leading to structural collapse in some cases. The female beetle may lay up to 200 eggs and if most of these hatch within the same structure, very substantial damage can be caused before the adult beetles emerge. The life cycle of the insect varies from 3 to 11 years.

The only other wood-boring species of major importance in Britain is the *Lyctid* family, the Powder Post beetle. This is exclusively a pest of recently seasoned hardwoods and feeds only on the sapwood portion. Although not particularly common in buildings, its damage to strip or block flooring or to fitted furniture is expensive to eradicate.

Preservation of timber against wood-boring insects is similar in principle to preservation against wood-decaying fungi, although insects are much larger than the exploring hyphae of a fungus. Moreover, an insect is mobile and has sensory organs so that it can exert some choice of deciding where to attack. Although tributyltin oxide is toxic to many species of insect, it is not really an effective insecticide in wood at the levels at which it is normally employed. For example, Baker and Taylor3 demonstrated that TBTO did not have any pronounced contact effect on adult Lyctus brunneus beetles or on the larvae of Anobium punctatum in wood. They considered that the action of TBTO was that of an effective stomach poison, i.e. it was necessary for treated wood to be "tasted" before a lethal dose could be absorbed. Because of this limited effectiveness, TBTO is often combined with powerful contact insecticides, particularly chlorinated hydrocarbons. It has been shown<sup>23</sup> that the fungicidal action of tributyltin oxide may be increased synergistically by the addition of these compounds; moreover, the effectiveness of the hydrocarbon as an insecticide is very much increased. Table 2 shows the increased fungicidal activity of TBTO in the presence of chlorinated hydrocarbons.

In many parts of the world termites are a major insect pest, being responsible for extensive damage to wood and fibre products. A paper by Nicholas and De Ryte<sup>24</sup> described the effectiveness of a combination of TBTO and dieldrin, a chlorinated hydrocarbon, in preventing termite attack in laboratory studies and in accelerated field tests. Again, synergism was evident in the insecticidal activity, as Table 3 shows.

A sample impregnated with a solution containing 0.5 per cent of dieldrin and 0.5 per cent of TBTO showed no evidence of termite attack even after more than three years of exposure, and the authors concluded that this formulation should constitute an effective long-term preservative treatment for wood against subterranean termite attack.

#### Methods of application of preservatives

#### Refs, 25-27

Organotin wood preservatives are normally applied to wood in organic solvents, although, as will be described later, there have been some developments with waterbased systems. Presenting the biocide in the most Table 2

Synergism of the fungicidal action of tributyltin oxide with chlorinated aromatic hydrocarbons

Salvart	Limiting conce	ntration of TBT fungi (%)	O against test	Mycelial growth of Coniophora cerebella a
	Alternaria tenius		0.01% TBTO (mm)	
Acetone	0.1	0.01	0.1	18
50% acetone with 50% o-dichloro- benzene*	0.001	0.001	0.001	
o-dichlorobenzene p-dichlorobenzene				9
p-chlorotoluene				10

\*o-dichlorobenzene shows no fungicidal action in mixtures with acetone

 Table 3

 Effectiveness of various treatments in field tests

Treatment	Solvent	Rating (pentachloro- phenol = 1)
Pentachlorophenol	solvent 2*	1
Toxaphene	solvent 325 <sup>†</sup>	3
Tri-n-butyltin oxide Tri-n-butyltin oxide/	solvent 325 <sup>+</sup>	5
lindane	solvent 325 <sup>+</sup>	10
Tri-n-butyltin oxide/		
dieldrin	solvent 325 <sup>†</sup>	30

\*An aromatic solvent Both solvents made by Standard Oil Co.

appropriate formulation and getting it to the correct location in the timber are perhaps as important as the choice of biocide itself. The most common methods of impregnation of treated timber are by total immersion or by pressure impregnation. Immersion techniques are perfectly satisfactory provided sufficient time is allowed for the solvent to penetrate the wood pores and transport the biocide to a sufficient depth for long-term protection; they are simple and inexpensive to operate. Vacuum and pressure impregnation systems involve greater capital cost, but allow the wood to be used fairly quickly after treatment. They also overcome problems with simple immersion treatments of variable absorbency in certain softwoods, when some regions tend to absorb excessive quantities of treatment fluid. There is a great variety of commercial processes, but the essential stages are similar in all cases<sup>9</sup>.

- 1. Load treatment cylinder with the wood to be treated.
- 2. Adjust the pressure of air trapped in the wood by applying a vacuum or pressure.
- 3. Flood the cylinder with treatment fluid and apply an impregnating pressure.
- 4. Drain the cylinder and adjust the pressure of air in the wood by applying a vacuum.
- 5. Return the timber to atmospheric pressure and unload.

These techniques are particularly suitable for pretreating in a standardised and reproducible manner, joinery made to strict dimensional tolerances. Specified treatments may be based on degree of retention of active agent, the required results in the treated product, or a standardised time of treatment; the latter is the one adopted by the UK National House Builders' Registration Council, which recommends a 3 minute immersion, or a corresponding standard impregnation cycle<sup>25</sup>.

For remedial treatment, obviously impregnation is not practicable. Treatment solutions are in these cases applied by brushing or spraying, the latter being preferred as being more convenient and allowing more even coverage. Care must be taken to avoid fire risk when spraying organic solvents in confined areas. One commercial product designed to overcome this risk contains the organic preservative as an emulsion and each solvent droplet is surrounded by a water film, reducing flammability. Paste formulations have also been produced and these will form a sealing skin on the surface, whilst the low viscosity preservative constituent migrates deep into the wood pores. These pastes are claimed to be effective in dealing with beetle infested wood.

One rather novel method of applying wood preservative has been developed under the trade name Woodcap by the Netherlands firm, Hoeka. The active fluid is contained in small sealed glass capsules which are inserted into bore

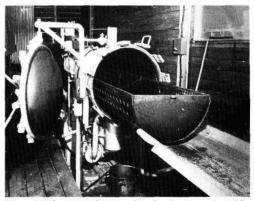


Figure 5. This pressure impregnation plant has been adapted for use with either solvent-based or water-based organotin preservatives. Photograph courtesy: Wykamol Ltd, Winchester

R in	w/v % solubility of compound ( $\pm 0.1$ )		
Bu <sub>3</sub> SnSO <sub>3</sub> R	After I day	1 month	2 months
Ph	0.2	0.5	0.6
C <sub>4</sub> H <sub>4</sub> Me-4	0.4	0.4	(1)
C,H,CI-4,NH,-5	0.06	(1)	(I)
C <sub>6</sub> H <sub>4</sub> Me-4 C <sub>6</sub> H <sub>3</sub> Cl-4,NH <sub>2</sub> -5 CF <sub>3</sub> Me	0.1	0.7	0.8
Me	1.1	≥1.6	≥1.6
Et	1.5	1.9	1.9*
n-Bu	0.8	0.8	0.8
t-Bu	0.7	0.8	0.8

 Table 4

 Water solubilities of Bu<sub>3</sub>SnSO<sub>3</sub>R compounds at 25°C

(I) = Not performed \*1.8% after 6 months.

holes (or at locations vulnerable to decay such as joints of frame-works) and then broken by sealing the hole with a wooden plug. The escaping preservative then gradually diffuses into the wood structure<sup>26</sup>. Subramanian *et al.*<sup>27</sup> have reported attempts to form organotin polymers *in situ* to protect wood. The wood is impregnated with an organotin vinyl monomer which subsequently polymerizes, giving, it is claimed, long-term protection by controlled release.

All wood preservatives are necessarily toxic substances, but no harmful effects will be experienced in the use of organotin-based formulations provided manufacturers' precautions are followed. Gloves should be worn during handling and eyes should be protected by goggles. If the solution is splashed on the skin, it should be washed off immediately with copious amounts of water. The UK Government's Health and Safety Executive operates a Pesticides Safety Precautions Scheme (PSPS) which has now been extended to cover wood preservative toxicants; products are examined by an advisory committee which makes recommendations regarding their use. Bis(tributyltin)oxide has been approved for use under this scheme in hydrocarbon solvents at levels of 3.0 per cent for industrial pre-treatment; and at 1.5 per cent for professional and 1.0 per cent for domestic timber treatments.

#### Water-borne organotin preservatives

#### Refs, 1, 6, 28-31

Water-based wood preservatives are widely used throughout the world and although organic solvent-based systems are preferred for many applications, e.g. pretreatment of joinery with strict dimensional tolerances, the water-based treatments are low in cost and do not introduce fire risks during application. To date, tributyltin compounds have not found wide use in water-borne systems because of their low water solubility (about 0.001 per cent). However, tributyltin oxide can be made water dispersible by the addition of suitable quaternary ammonium salts; these quaternaries are active against gram negative organisms, so that their incorporation also widens the range of effectiveness. These formulations were originally developed for treatment of algae growths on masonry<sup>28</sup>, but it was subsequently found that they were also highly effective as wood preservatives. In fact, the activity of tributyltin oxide against wood-destroying fungi appears to be enhanced in the presence of polar solvents and particularly in the presence of water. It has been speculated that this may be due to the ability of waterborne tributyltin compounds to penetrate into the walls of the wood cells, thus protecting them from enzymatic attack; organic solvent-borne organotins tend to be confined within the interior of the cells. Also, if active protein sites in the fungi involve free thiol groups, the organotin may combine more readily with these in an aqueous medium<sup>6</sup>.

A typical water-dispersed organotin concentrate contains 1 part tributyltin oxide, 8 parts of a quaternary ammonium compound such as benzalkonium chloride (50 per cent active agent) and 1 part water. This overall 10 per cent TBTO concentrate is then diluted with water to give any desired concentration of the organotin<sup>29</sup>. The first proprietary preservative to use this system was Permapruf T<sup>+</sup>. Results of long-term trials indicate that it is an efficient alternative to water-based copper-chromearsenate formulations, being effective at lower retentions of active ingredient in sapwood<sup>30</sup>. Pressure impregnation treatment vessels have been modified so as to be suitable for impregnation of timber with water-based organotins. The formulation has been approved for use in Sweden (under the name BP Hylosan PT) by the Swedish Wood Preservation Institute<sup>1</sup>.

Workers at the International Tin Research Institute have adopted a slightly different approach by synthesising discrete water-soluble tributyltin compounds. A systematic study of compounds of the type Bu<sub>3</sub>SnSO<sub>3</sub>R has been undertaken to study the effect of the R group on solubility<sup>11</sup>. Some of the results obtained are shown in Table 4. Aqueous solubilities of the tributyltin alkane sulfonates were in the range 0.7-1.5 per cent w/v which would be high enough for most biocidal applications.

A wood block agar test has been carried out on aqueous solutions of tributyltin ethanesulfonate against *Coniophora puteana* and *Coriolus versicolor*. The toxic limits (Table 1) were found to be similar to those for TBTO. This compound is currently being tested at Forintek Canada Corporation as an aqueous biocide using the American Wood Preservers' Association (M-10) test.

#### The future for organotin wood preservatives

Organotin compounds are well-established as wood preservatives, with TBTO having over 20 years of use in this field. The use of this compound has revolutionised the pre-

<sup>†</sup>Trade name, Wykamol Ltd, Winchester

#### 1981(6) ORGANOTINS IN WOOD PRESERVATION

treatment of building timbers, with guaranteed protection of the wood and no undesirable side effects. As has been shown in this review, other organotin compounds are now being studied, at the International Tin Research Institute and elsewhere, which may prove even more effective. In addition, much more information is being gathered on mechanisms of decay and the means by which this is prevented, which may help in eventually "tailoring" compounds for protection under particular conditions of use of the wood. The concept of water-soluble organotin preservatives could open up a whole new field of applications for these compounds. All in all, there seems to be an exciting future ahead for organotin-based wood preservatives, with consequent benefits to all, as all are dependent upon the use of timber in one form or another.

#### Acknowledgements

The authors would like to thank the International Tin Research Institute for permission to publish this paper.

Received 23 February 1981

#### References

- 1. King, S., Tin and its Uses, 1980, 124, 13.
- 2. Int. Tin Res. Inst. Publcn. L 65.
- 3. Baker, J. M. and Taylor, J. M., Ann. Appl. Biol., 1967, 60, 181.
- 4. Hof, T., J. Inst. Wood Sci., 1969, 4, 19.
- 5. Richardson, B. A., Recd. Brit. Wood Preserv. Assn., Ann. Conven., Cambridge, 1970, 37.
- 6. Crowe, A. J., Hill, R. and Smith, P. J., Int. Tin Res. Inst. Publicn. 1978, 559.
- 7. Crowe, A. J., Hill, R., Smith, P. J. and Cox, T. R. G., Int. J. Wood Preserv., 1979, 1, 119.
- 8. Wood preservatives approved by the Swedish Wood Preservation Institute, Svensk., Traskyddsinst., Stockholm, 1979.
- 9. Richardson, B. A., "Wood Preservation", Construction Press, 1978.

- 10. Dinwoodie, J. M., Composites, 1971, Sept.
- 11. Dickinson, D. J. and Levy, J. F., Recd. Brit. Wood Preserv.
- Bravery, A. F., Proc. Sessions on Wood Products Pathology, of 2nd Internat. Congress of Plant Pathology. 1973, 33.
- 13. Bravery, A. F., Proc. Conf. Int. Symp. Berlin, 1975; Mater. u. Organismen Chem. Suppl., 3, 331. 14. Richardson, B. A. and Lindner, G. H., 2nd Penarth Conf.,
- Cambridge, 1979, p. 12.
- 15. Smith, P. J., Crowe, A. J., Allen, D. W., Brooks, J. S. and
- Formstone, R., Chem. Ind., 1977, 5 Nov., 874.
   Bravery, A. F., Parameswaran, N. and Liese, W., Mater. u. Organismen Chem., 1975, 10, 31.
- 17. Aldridge, W. N., Am. Chem. Soc., Adv. Chem. Ser., 1976. 157, 186.
- 18. Kaars Sijpesteijn, A., Luijten, J. G. A. and Van der Kerk. G. J. M., ed. Torgeson, D. C., "Fungicides, an advanced treatise", Vol. II, Academic Press, New York, 1969, 331. treatise"
- 19. Smith, P. J., 22nd German Tin Day 1978, Special issue of Rev. Organometall. Chem., Si Ge, Sn and Pb, 1980.
- 20. Bravery, A. F., Internat. Biodeter. Bull., 1979, 6, 145.
- 21. Henshaw, B. G., Laidlaw, R. A., Orsler, R. J., Carey, J. K. and Savory, J. G., Recd. Brit. Wood Pres. Assn., Ann. Conven., Cambridge, 1978, 19.
- Wright, P. S., J. Dentistry, 1980, 80, 144.
- 23. Thust, U., Tin and its Uses, 1979, 122, 3.
- 24. Nicholas, D. and De Ryte, R., Recd. Brit. Wood Pres. Assn., Ann. Conven., Cambridge, 1972, 129.
- 25. Brooks, F. W., Recd. Brit. Wood Pres. Assn., Ann.
- Woodcap", Tech. Note, Hoeka Sier pleisters en Muurverven BV, (PO Box 88, 5750 AB Deurne, The 26. Netherlands).
- 27. Subramanian, R., Proc. 5th Internat. Symp. Controlled Release Bioactive Materials, Washington DC, 1978.
- 28. Richardson, B. A., Stone Ind., 1973, 8 (2).
- 29. "TBTO in water-based preservatives for wood", Albright and Wilson Ltd, Tech. Service Note TS/RECH/C5, 1975.
- 30. Richardson, B. A. and Cox, T. R. G., Tin and its Uses, 1974, 102, 6.
- 31. Blunden, S. J., Chapman, A. H., Crowe, A. J. and Smith, P. J., Internat. Pest Control, 1978, 20, 5.

## Recent formulation developments in chlorinated rubber paints

#### By R. G. Humphries

Imperial Chemical Industries Limited, Mond Division, PO Box 13, Runcorn, Cheshire WA7 4QF, England

#### Keywords

Raw materials for coatings binders (resins etc.)

> chlorinated rubber resin

#### Introduction

Chlorinated rubber has been commercially available as a paint resin for the past 40 years. Initially it was used in low build chemical resistant finishes and pool paints and built up a reputation as a trouble shooter due to its ability to give good results where other systems had failed.

During the early 1960s with the concept of high build paints being accepted by the industry, better standards of surface preparation and more rapid methods of application using airless spray, the product showed remarkable growth and is today one of the most important resins for high performance coatings.

This paper describes some of the more recent projects carried out in the laboratories at ICI Mond Division and highlights the benefits that can be achieved in primers, high build coatings and finish paints by modifying with other resins.

The paper reviews recent developments in chlorinated rubber paints concentrating on the benefits which can be achieved particularly in primers and finishes by modifying with other resins.

#### **CR/micaceous iron oxide paints**

Micaceous iron oxide is one of the traditional paint pigments and has been used on bridges since the beginning of the century. CR/MIO (chlorinated rubber/micaceous iron oxide) paints have given very good results in aggressive industrial atmospheres, and have found application in marine paints, on drilling rigs, bridges, electricity pylons and gas installations.

One of the defects commonly noted with darkly pigmented CR formulations, such as those containing MIO, is the development of fine cracks on the paint surface known as checking. The phenomenon is normally attributed to differential film hardness, and has been noted on exterior exposure panels particularly in subtropical climates.

A more recent investigation of this checking phenomenon led to the proposal that checking was yield failure of the outermost skin of a paint film, caused by stresses set up during drying. Solvents can diffuse faster from the surface of black pigmentations under sunlight, due to higher surface temperatures attained, and the effect of temperature on diffusion rate is known to be great for

224

Miscellaneous terms

formulation

plasticized CR films at ambient temperatures. In the early stages of paint drying, the stresses created simply cause convection flow. However, once the paint sets, if the surface cannot stand the stress it contracts to produce a checked pattern.

The investigation demonstrated that checking normally occurred very early after outdoor exposure, usually in the first two months. In addition, reducing the blackness of paints by the incorporation of minor amounts of metallic or white pigments reduced the tendency to check. Paint films which were stoved to eliminate retained solvent prior to exposure did not check.

Increasing the yield value of the partially dried paint film should therefore also reduce the tendency to check. Trials carried out have demonstrated that a reduction of plasticizer level and increasing pigment concentrations have a major effect. Faster drying solvents also proved beneficial. Thus the CR/Cereclor 42 ratio 70:30 was better than 65:35 and the CR/Cereclor 70/Cereclor 42 ratio 55:35:10 was better than 50:33:17. Forty per cent PVC MIO was better than 30 per cent. Xylene was the best solvent. The two best paints, which showed no signs of checking after 10 months exposure in the UK and in Johannesburg, contain all the features mentioned:

	11G649	11G645
Alloprene R10	12.9	11.5
Cereclor 70		7.3
Cereclor 42	5.5	2.1
Thixomen	1.1	1.1
MIO	43.3	45.8
Xylene	37.2	32.5
PVC	40%	40%
Viscosity 10,000 s <sup>-1</sup>	1.0P	1.0P
Binder	R10/C42	R10/C70/Cer 42
	70:30	55:35:10

#### **CR**/epoxy blends

Modification of epoxy paints with CR has proved a novel but effective method of overcoming an inherent defect of poor intercoat adhesion.

Laboratory tests have shown that CR is fully compatible with Epikote 828, Epikote 834 and Epikote 1001, provided a proportion of polar solvent is present in the solvent blend. The choice of hardener is a little more critical, due to the fact that CR reacts vigorously with the colourless amine and polyamide hardeners normally used. However, the less basic, but unfortunately highly coloured aromatic amines, have proved effective crosslinking agents whilst not reacting too strongly with the chlorinated rubber.

An 8 per cent PVC paint was chosen to demonstrate the improvements in intercoat adhesion by modification with CR.

CR/epoxy (red oxide)	28G697	CR/epoxy pitch	28G629
Epikote 828	26.2	Epikote 828	20.4
Alloprene R10	19.7	Alloprene R10	10.2
Thixomen	1.0	Special pitch 5	27.2
Microtalc	2.2	Red iron oxide	6.3
Red iron oxide	7.0	Asbestine 325	4.4
Barytes	6.5	Microtalc	2.1
Xylene	29.9	Silicone resin 281	0.4
Solvesso 100	7.5	6% zinc naphthenate	1.7
		Thixomen	0.6
Ancamine LT	13.1	Xylene	21.4
		Solvesso 100	5.3
		Ancamine LT	10.2
PVC	. 8%	PVC	8%
Viscosity 10,000 s <sup>-1</sup>	2.0 P	Viscosity 10,000 s <sup>-1</sup>	1.6 P

The paints are prepared by dispersing the pigments and extenders in a solution of the epoxy resin with a high speed cavitation mixer. The CR is dissolved in a part of the solvent blend to give a 40 per cent w/w solution. The thixotropic agent is incorporated into the CR solution by stirring until a temperature of  $48-55^{\circ}$ C is reached; the resulting gelled lacquer is added, whilst stirring, to the epoxy millbase. The hardener is added just before use.

#### Laboratory tests

#### Intercoat adhesion

The CR/epoxy modified paints were weathered for three months at an industrial weathering station and cleaned with water before overcoating. Unmodified epoxies were included as controls. The CR/coal tar epoxy paints had been weathered for six months before overcoating.

System	Elcometer adhesion	Cross hatch/sellota (BS 3900 Pt E6)	
Unmodified epoxy	100% intercoat adhesion failure at low "pull off" pressures. 10 psi	total failure	(5)
Coal tar epoxy	100% intercoat at 10 psi	total failure	
CR/epoxy	Mixed failures (70% cohesive of top coat) 250 psi	good adhesion	(0)
CR/coal tar epoxy	100% intercoat at 100 psi	fair/poor adhesion	
0 = Good ahesi 5 = Poor adhes			
Konig rocker h	ardness		
CR/epoxy Unmodified epoxy		80 90	

#### Weathering data

The test paints were exposed for three years at the following sites:

> Holford – Cheshire Gladstone Dock – Liverpool

In addition the CR/coal tar epoxy paint has been on a test raft in the Menai Straits for two years. No failures of any kind have been reported during this period.

#### Chlorinated rubber/tar blends

Blending CR with coal tar gives the paint formulator an opportunity to upgrade the cheaper coal tar fractions by blending with a sophisticated high performance resin. The resultant paint has rapid drying properties, adequate chemical resistance and reasonable impermeability all conferred by the CR, whilst the coal tar gives improved wetting properties, increased volume solids and is comparatively cheap by todays standards.

The paints are suitable for:

- 1. Ballast tanks, underwater hulls and double sections.
- Land based coatings, where colour and appearance is of lesser importance e.g. undersides of bridges and certain storage tanks.
- 3. Vehicle underseals and sound deadening compositions in the automotive industry.

The tar should be compatible with Alloprene and other binder constituents and those with low phenol, low sulphur and low nitrogen contents have proved to be the best candidates. In addition the tar should be relatively free of volatile materials which could act as plasticizers. Most of the work has been carried out with special pitch 3 ex BSC and its solutions in xylene special pitch 4 (90 per cent w/w) or special pitch 5 (85 per cent w/w).

The table below gives two recommended starting formulae.

	Mond reference	
	17G562	17G507/1
Alloprene R10	9.8	8.9
Special pitch 5 (85% solids)	16.4	17.5
Cereclor S52	3.5	3.7
Hydrocarbon resin LMS4500	0.7	2.3
Thixomen	1.5	1.5
Micronised red iron oxide	28.7	14.7
Micronised barytes		14.8
Microtalc AT1	9.7	10.0
Araldite CY 179	0.5	
Zinc naphthenate	1.5	
Epichlorohydrin		0.1
Zinc oxide		1.0
Xylene	20.2	18.9
C, Aromatic hydrocarbon	7.5	6.3
PVC	30%	30%
% vol solids	48	48

#### **Details of paint formulation**

#### Binder

R10/special pitch/Cereclor S52/hydrocarbon resin within the range  $35:50:12.5:2.5 \rightarrow 30:50:12.5:7.5$  w/w.

The Cereclor S52 gives improved flexibility and adhesion whilst the hydrocarbon resin improves compatibility between the CR and the tar and also gives a more abrasive resistant coating.

#### Pigmentation

20 per cent VC red iron oxide/10 per cent VC microtalc or 10 per cent red iron oxide/10 per cent VC microtalc/10 per cent VC barytes.

#### Solvent

Xylene/C, hydrocarbon 3:1 w/w.

#### Stabilisers

The use of auxiliary stabilisers is most important especially where storage in high ambient temperatures is involved. Of the many stabilising systems studied, the best results were obtained with zinc naphthenate/Araldite CY179 (zinc naphthenate, 1 per cent w/w solids on CR; Araldite CY179, 0.5 per cent w/w on paint; or zinc oxide, 1 per cent w/w on total paint).

#### Performance

Formulations based on the above binders have now been on exposure at both rural and industrial weathering sites and are still performing well after seven years. Another series has been on exposure on a marine raft in the Menai Staits for over six years and is still in very good condition. For both industrial and marine exposures the system tested was:

Blast clean Sa $2\frac{1}{2}$	
Zinc rich epoxy	30µm
$2 \times CR/tar$ composition	200µm
total dft (dry film thickness)	230µm

#### **CR**/acrylics

The last decade has seen a rapid increase in the demand for chlorinated rubber, particularly in the industrial maintenance sector. Today the use of CR paints is no longer restricted to the protection of chemical plants and other aggressive environments but is finding increasing use in the protection of bridges, docks and harbour installations, sewage plants, refineries, and containers where cosmetic properties are very important.

CR is compatible with a wide range of commercially available acrylics. Paints produced from a blend of chlorinated rubber/acrylic and modified, for example with an inert chlorinated paraffin plasticizer, have produced paints with a number of distinct advantages.

1. Improved light stability: choice of solvent is also an important factor in light stability and for best results the level of  $C_{q}-C_{10}$  aromatic hydrocarbons should be kept to a minimum.

- Tougher films which show greater resistance to checking and crocodiling.
- 3. Have better solvent release properties making them candidates for offsite application.

Acrylic modification does not seriously downgrade the chemical resistance of chlorinated rubber and these paints are suitable for all but the most aggressive chemical environments. Airless spray application properties have also been examined and satisfactory results were obtained with Neocryl B725 (a poly-methacrylate copolymer from Polyvinyl Chemie), Paraloid F10 (a thermoplastic acrylic from Rohm & Haas) and Acronal 4F (a low viscosity butyl polyacrylate from BASF). This list is by no means exhaustive and there may be many others which are suitable. Ratios examined included 3:1, 4:1, and 6:1 w/w ratio of CR/acrylic. Natural weathering in South Africa and the UK produced very little difference between the ratios except that those containing the higher levels of acrylic were slightly less prone to yellowing.

#### **Typical CR/acrylic formulations**

	High build	Finish	
	15G549	15D554/2	
Alloprene R10	14.2	17.4	
Acronal 4F	4.7	5.9	
Cereclor S52	4.7	5.9	
Tioxide RCR 2	7.4	14.9	
Barytes	23.8		
Thixomen	1.0	0.5	
Soya lecithin	0.3		
Xylene	35.1	33.3	
Solvesso 100	8.8	16.6	
Butyl ethoxol		5.5	
PVC	30%	16.0%	
Viscosity 10,000 s <sup>-1</sup>	1.8P	1.0P	

#### Alloprene/hydrocarbon resin blends

Alloprene is compatible with a wide range of hydrocarbon resins particularly those of an aromatic character. It is less compatible with the aliphatic hydrocarbons but this can be overcome by using a third component, e.g. chlorinated paraffin, which acts as a compatibilising agent and plasticizer. Inclusion of hydrocarbon resin in a chlorinated rubber based paint gives:

- 1. higher volume solids (45-50 per cent)
- 2. improved film hardness
- 3. cheaper formulations

As the resins are inert, chemical resistance is not downgraded but the formulator should be aware that certain of the HC resins tend to yellow quite badly. This is not the case with the aliphatic hydrocarbons such as Imprez 100.

During the past 10 years several evaluations of CR/hydrocarbon resin blends have been carried out in ICI's laboratories. Hydrocarbon resins studied have included:

 Necires EPX Necires ALX-100 (can also act as a plasticizer) in compositions corresponding to:

	Alloprene R10	20-50 per cent w/w binder
	Necires EPX	40-80 per cent w/w binder
	Cereclor S52 or Necires ALX 100	5-10 per cent w/w binder
2.	Hercures AL65	

A80 A100

> A120 Stabelite Ester 10 Imprez 100 in compositions corresponding to

Alloprene R10	41-52 per cent w/w binder
Hydrocarbon resin	13-31 per cent w/w binder
Cereclor 42	28-35 per cent w/w binder

3. Escorez 8090

in compositions corresponding to:

Alloprene R10	30-60 per cent w/w binder
Escorez 8090	15-37.5 per cent w/w binder
Cereclor 42	20-32.5 per cent w/w binder

Paints were formulated to a total PVC of 30 per cent using either barytes/Tioxide 2:1 v/v or red iron oxide/barytes/talc 1:1:1 v/v.

Laboratory testing testing salt water soak, accelerated weathering and salt spray whilst natural weathering tests were carried out at rural and industrial weathering stations. In addition certain series were subjected to underwater immersion on a raft in the Menai Straits.

The most promising binder ratios from these series were as follows:

#### Alloprene R10/Necires EPX/Cereclor S52 50:40:10 w/w

This ratio will require modification to overcome the checking evident after five years natural weathering. This could be overcome by reducing the flexibility of the binder and slightly increasing the PVC. The paints did well for the first two years on underwater immersion but the degree of breakdown was quite advanced after four years.

#### Alloprene/Hercures and Alloprene/Stabilite Ester 10

After seven years exposure, signs of checking were evident, although the results are better than those observed with the Necires. This series was not exposed on the test raft.

#### Alloprene/Imprez resin

Most promising ratios were R10/Imprez 100/Cereclor S52 48:32:20 and 52:35:13 w/w. This series has also been on exposure for seven years with no signs of checking. Not exposed on test raft.

#### Alloprene/Escorez resins

Best ratios R10/Escorez/Cereclor S52 60:25:15. Similar to the results obtained with Imprez after three years exposure.

#### **CR/alkyd blends**

These are amongst the most versatile of the CR paints currently in commercial use, being particularly suitable for:

- (a) maintenance primers
- (b) offsite painting

#### Maintenance primers

Oil based paints containing inhibitive pigments are accepted as being the most tolerant to poorly prepared surfaces. The oil forms soaps and azelates which inhibit corrosion of the steel surface. CR is compatible with a wide range of alkyds and oleoresinous varnishes, and blends of CR with these dry rapidly (an important asset when more than one coat has to be applied in a day), are . less permeable to water and moist corrosive gases, and have much improved chemical resistance. The soap formation, wetting and adhesion of the alkyd or varnish is not imparied. Good general purpose maintenance primers can be based on blends of CR/alkyd, CR/oleoresinous varnish or CR/oils. These primers have been on test at an industrial exposure site since 1974 on both blast cleaned and wire brushed steel and are still performing very well.

The following formulations are suitable for brush application giving dft's around  $25-35\mu$ m per coat. They can be overcoated with a normal CR high build after 24 hours drying.

#### **Typical formulations**

CR/oleoresinous primer 16A480	% w/w	CR/alkyd primer 16A656	% w/w
Alloprene R20	12.6	Alloprene R 10	15.0
Linseed tung varnish	16.9	Uralac 151 (100%)	7.6
(75%)		Cereclor 42	3.8
Zinc phosphate	22.3	Zinc phosphate	20.4
Zinc chromate	5.8	Tioxide RCR 2	7.4
Red iron oxide	2.8	Microtalc	7.3
Microtalc	6.4	Yellow iron oxide	0.2
Thixomen	0.5	Soya lecithen	0.2
C <sub>o</sub> hydrocarbon	25.8	Thixomen	0.7
White spirit	6.5	Methyl ethyl ketoxime	0.1
Driers/100 varnish		C <sub>a</sub> aromatic	
solids		hydrocarbon	29.6
Lead	0.5	White Spirit	7.3
Cobalt	0.05	The second s	
PVC	35%	PVC	34%
Viscosity 180 s <sup>-1</sup>	5P	Viscosity 180 s	7P

#### CR/alkyds for offsite painting

It is becoming increasingly popular to apply a substantial quantity of paint to steel, prior to erection. This procedure permits paints to be applied under factory conditions where drying temperatures can be controlled and the problem of intercoat contamination reduced. Furthermore, all parts of the steel, even those which become inaccessible after erection, can be properly protected.

Any damage caused to the paint system during transportation is touched up on site followed by application of the final coat. Three basic requirements are essential for successful offsite application:

- The paint must dry quickly to facilitate rapid overcoating, essential if acceptable throughput of steel is to be achieved.
- The paint film must achieve its maximum toughness quickly to permit early handling of the steel without causing undue damage.
- The paint must be overcoatable for periods ranging from a few hours to perhaps two years and not exhibit intercoat adhesion problems.

A conventional CR system, i.e. plasticized with chlorinated paraffin, certainly meets the first two requirements and in fact has been successfully used within ICI's Agricultural Division.

The current Agricultural Division specification for new steel structures is:

#### Offsite

Blast clean	Sa 2+ (	Swedish Standard 055900 1967)
1 × zinc rich	epoxy	35µm
$I \times CR$ high	build	75µm

#### After erection

$1 \times CR$ high build	75µm
Total dry film thickness	185µm

This system performed so well that it has now been adopted for all new steel within the Agricultural Division Unmodified CR paints are also used in offsite painting of motorway pedestrian bridges and overhead gantries, although in this instance lifting hooks are fitted to facilitate handling.

Although the pure CR paint as indicated is performing satisfactorily there is a need to develop a CR based coating which attains a tougher film more rapidly. Of the modifying resins studied, the best results were obtained with alkyds, epoxy esters and acrylics. Starting formulae and some test results for the alkyd variants are discussed below. The acrylic formulations have been discussed previously and the epoxy ester formulations follow in the next section.

Most of the initial development work was carried out using Plastokyd 601X a DCO modified short oil alkyd from Croda Resins Ltd. Preliminary tests had shown this resin, in combination with CR, to be capable of fulfilling the requirements of rapid drying to give much harder films than the traditional CR/chlorinated paraffin blends.

Paints were prepared to the following general specifications:

- Binder: Plastokyd 601X, Alloprene, Cereclor 42 at ratios varying from 4:1:0 → 1:2:0.5 w/w.
- Pigmentation: zinc phosphate 23 per cent VC, zinc chrome 5 per cent VC, Tioxide RCR2 6.3 per cent VC, total PVC 35 per cent.
- Solvent blend: xylene/C<sub>9</sub> aromatic hydrocarbon 4:1 w/w (airless spray) or C<sub>9</sub> aromatic hydrocarbon/white spirit 4:1 (brush)

#### **Test results**

Scratch hardness BS 3900 Pt E2	1000 g/25µm dft (24 h) 2000 g/25µm dft (7 days)	rating
Salt spray	2 × 30µm dft primer	
BS 3900 Pt F4	clean steel (Sa $2\frac{1}{2}$ )	9 7
4000 h	rusty steel (St 2)	7
	$1 \times 30 \mu m$ dft primer + $1 \times 30 \mu m$	
	CR finish (Sa 2 <sup>1</sup> / <sub>2</sub> )	10
	(St 2)	6
Humidity	$2 \times 30 \mu m$ dft primer	
BS 3900 Pt F2	clean steel (Sa $2\frac{1}{2}$ )	6
4000 h	rusty steel (St 2)	6
	$1 \times 30 \mu m$ dft primer + $1 \times 30 \mu m$	-
	finish (Sa $2\frac{1}{3}$ )	6
	(St 2)	6

There was no appreciable difference in the anticorrosive properties of the binders within the range 4:1 Plastokyd  $601X/CR \rightarrow 1:2$  Plastokyd 601X/CR. Increasing the PVC from 30 per cent to 40 per cent did not significantly downgrade the performance.

#### Overcoating

The painting of new steel structures necessitates a range of overcoating times, varying from a few hours under controlled factory conditions to perhaps two years when the final coat is applied on site. Table 1 shows the trends obtained when overcoating CR/alkyd primer undercoat

Alkyd/CR ratio and PVC	4:1 3:	5%	4:14	0%	2:1 3	5%	2:1 4	0%	1:2 3	5%	1:2 40	0%
Blast primer	PVB	E ·	PVB	Е	PVB	E	PVB	E	PVB	E	PVB	E
Overcoating interval												
4 hours I day	S S S	S	S S									
7 days 14 days	S	L	S	L		L		L				
21 days 28 days		L L		L L		L L		L				
56 days		severe L		severe L		severe L		severe L				
Key: PVB E	– polyvinyl t – epoxy poly				L S	— liftir — slipj	ng ping		"blank"	– OK		

Table 1 Overcoating of Alloprene/Plastokyd 601X primer undercoats

0/ ..../....

with a typical CR high build. Variables studied include types of blast primer, CR/alkyd ratio, PVC of the primer undercoat and interval between application of the primer and high build.

#### System:

- 1. Mild steel panels blast cleaned to Sa  $2\frac{1}{2}$  of Swedish Standard SISO559 00-1967.
- Polyvinyl etch primer or epoxy polyamide primer 10μm.
- 3. 1  $\times$  experimental primer undercoat (brushed) 35µm.
- 4. 1  $\times$  CR MIO high build (airless sprayed) 100 $\mu$ m.

In all cases the primer undercoat was softened by the MIO high build and in fact slipping was observed with some of the alkyd rich undercoats, but only over the PVB blast primer. Table 1 is self explanatory and shows that for trouble free overcoating the alkyd/CR 1:2 ratio was by far the best of the three ratios studied.

Formulation details are given below:

Mond ref. 14A489/2

% W/W
14.0
14.0
3.4
22.2
5.2
7.2
0.4
1.5
32.1
35%
1.6P

#### Impact and adhesion

Falling ball impact BS 3900 Pt E7	No loss of adhesion over 1 and 2 pack etch primers PVB etch primers, zinc rich epoxy or epoxy iron oxide
Cross hatch adhesion BS 3900 Pt E6	Good adhesion (rating 0)

0 = good 5 = bad

#### **Exposure** data

These primers have been on exposure for one year at three different sites in the UK including Widnes (heavy industrial), Peckforton (rural), and Teesside (heavy industrial) in the North East. A stepped build up system was used (typical of many UK bridge specifications) involving:

blast primer 3 × primer undercoat CR/MIO high build	25μm (CR/alkyd type) 120μm 80μm
CR finish	25µm
total dft	250µm

This has enabled an assessment of the performance of single as well as multiple coats in the system. After one year weathering the single  $25\mu m$  coat of blast primer was showing about 50 per cent breakdown but the remaining sections were still in perfect condition. The exposure tests are continuing.

Although the initial development work was carried out using Plastokyd 601X alternative alkyds which can be used include:

Uralac P470	<ul> <li>a medium oil soya alkyd</li> </ul>
Uralac 151	<ul> <li>linoleic rich, pentaerythritrol, 65 per cent fatty acids</li> </ul>
Uralac 211	<ul> <li>linoleic rich, glycerol, 55 per cent fatty acids</li> </ul>
Mitchalac 203	- DCO alkyd, glycerol/phenolic
	<ul> <li>linseed DCO, pentaerythritol, 75 per cent fatty acids</li> </ul>
Alftalat AR351	- DCO, 33 per cent fatty acids

CR/alkyds are also well established in applications such as: marine superstructure paints, fire retardant paints, agricultural machinery and traffic paints.

#### **CR**/epoxy esters

Epoxy ester based paints dry quickly to give tough, hard durable films ideal for primer/undercoats in offsite applications. Overcoating, particularly with paints containing strong solvents, can be a problem and in the case of chlorinated rubber lifting and rivelling can be a problem even after the primer has been applied for periods of up to six months. Development projects carried out have shown that paints based on CR/epoxy esters retain the fast build up of film hardness, whilst overcoming the overcoating problems mentioned previously. As with the alkyd modifications discussed previously, CR is the main component of the binder and the small amount of additional plasticizer necessary to achieve the required flexibility, also ensures complete compatibility between the CR and the epoxy ester.

The formulation suggested below has resulted from a programme of work involving three short oil DCO epoxy esters.

Mitchalac 694X	60 per cent w/w in xylene ex
– a DCO ester	Warwick Chemicals
Synolac 463X – a DCO ester	60 per cent w/w in xylene ex CVP
Plastokyd ED4X	50 per cent w/w in xylene ex
– an epoxide ester	Croda Resins

Mechanical tests on detached films using an Instron tensile testing machine, indicated an optimum ratio for CR/epoxy ester/chlorinated paraffin of 53:27:20.

Using this binder and a zinc phosphate/zinc chromate pigment, primer undercoats where prepared and subjected to the following tests:

- overcoating with CR high build
- scratch hardness (BS 3900 pt. E2)
- cross hatch adhesion (BS 3900 pt. E6)
- elcometer adhesion and falling ball impact (BS 3900 pt. E7)
- accelerated and natural weathering tests.

\*The addition of 1 per cent maleic or benzoic acid, calculated on total pigment, has proved an effective stabiliser against viscosity increase caused by reaction between the high acid value alkyd and the basic pigments.

Comparisons were made with a traditional CR/chlorinated paraffin primer at a 70:30 w/w ratio.

#### Scratch hardness

Paint type	Load to failure in g for a 25µm dry film after								
	24 h	7 days							
CR/Cereclor 42	700	1000							
CR/epoxy ester	1000	2200							

#### Adhesion tests

Systems tested:

4 mm steel, blast cleaned to Sa  $2\frac{1}{2}$  Swedish Standard

20µm dry blast primer (1 and 2 pack polyvinyl butyral, zinc rich epoxy iron oxide)

 $2 \times 60 \mu m$  CR/epoxy ester primer undercoat.

The panels were dried for 7 days before testing.

Paint type	Cross hatch	Elcometer
CR/Cereclor 42	0	cohesive primer undercoat
CR/epoxy ester	0	cohesive primer undercoat

 $0 \times \text{good} 5 \times \text{bad}$ 

Falling ball impact 0°C, system tested:

Same as for the previous tests except that the panels were conditioned for 2 hours at 0°C immediately before impact tests were carried out.

Paint type	Impact result* (1 or 2 pack etch primers only)						
CR/Cereclor 42	poor adhesion						
CR/epoxy ester	no loss of adhesion						

\*Over the zinc rich epoxy and epoxy iron oxide all systems performed satisfactorily.

#### Overcoating

All paints overcoated satisfactorily with a CR high build coating after intervals of time varying between 2 hours and 6 months.

#### Weathering

These primers were exposed at 3 different sites in the UK including Widnes (heavy industrial), Peckforton (rural), and Teesside (heavy industrial) in the North East.

The systems used were exactly the same as those described in the "CR/alkyd blends" section previously.

After one year of weathering the single 25µm coat of CR epoxy ester exhibited very slight breakdown, but the remaining sections were still in perfect condition.

#### Typical epoxy ester formulation

18E569	% w/w
Alloprene R10	13.2
Mitchalac 694X	11.0
Cereclor 42	5.8
Zinc phosphate	20.3
Tioxide RCR-2	7.4
Microtalc AT1	7.3
Yellow iron oxide	0.6
Soya lecithin	0.2
Bentone 34	0.2
Industrial methylated spirits	0.1
Methyl ethyl ketoxime	0.1
Solvesso 100/white spirit, 4:1	33.8
PVC	36%
Viscosity 10,000 s <sup>-1</sup>	2.5P

#### Acknowledgements

The author would like to thank his colleagues A. J. Burgess, D. Caldwell and C. A. Wyld for their assistance in the preparation and writing of the above paper.

Received 6 February 1981

## Next month's issue

The Honorary Editor has accepted the following papers for publication. They are expected to appear in the July issue of the *Journal*:

An experimental study of cavitation in real ink systems using temperature measurement techniques by M. S. Ozogan and F. R. Young

**Crystal chemistry of molybdenum red and orange pigments** by M. L. Somme-Dubru, M. Genet, E. Buyse, H. Margolin, W. Kondrachoff and P. G. Rouxhet

Problems involved in determining the solids content of amino resins, taking melamine resins as an example by R. Stange, L. Klug and H. Klug

Waterborne acrylics and urethanes for the coatings industry by H. van de Wiel and W. Zom



## Control the surface characteristics of your paint with Celite<sup>®</sup> extenders and flatting agents from Johns-Manville.

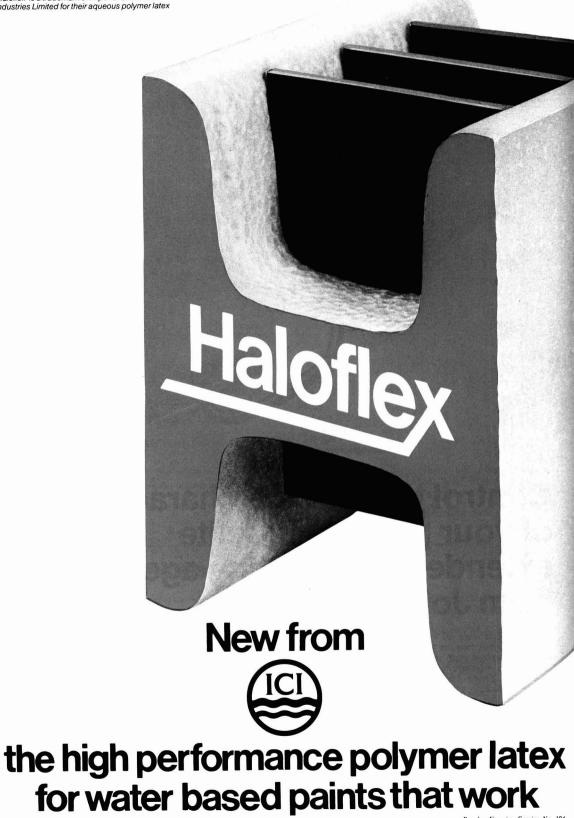
With Celite extenders you have complete control, from flat to gloss, depending on how much you add. They're pure, inert and non-reactive diatomaceous silica. Their high flatting efficiency results in uniform gloss and sheen reduction, from a silky semigloss to dead flat.

Celite extenders are available in several grades for both solvent and

water-thinned paints. These grades give you the flexibility you need depending on your formulations, desired degree of gloss and sheen reduction, type of dispersion equipment and the desired degree of final film smoothness (up to 5 Hegman fineness).

Johns-Manville Technology has been at work in the paint industry for over 30 years. Let us help you. Contact Johns-Manville Great Britain Ltd., Parkbridge House, The Little Green, Richmond, Surrey, TW9 IQU, Great Britain, Telex: 928635.

# **Johns-Manville**



## With Haloflex' you can make water based paints which protect steel *effectively* in aggressive conditions

## Just send for these coated steel panels and prove it yourself

"Haloflex' sounds interesting. Please send me coated test panels and literature.

Name	 	
Position	 	 
Company	 	
Address		

Samples of latex and paint are also available.



'Haloflex' sounds interesting. Please send me coated test panels and literature.

Name\_

Position.

Company

Address\_

Samples of latex and paint are also available.



## Other exciting possibilities for 'Haloflex'

While its use as an aqueous polymer latex for water based paints is the most promising and immediate application for 'Haloflex', research findings indicate valuable potential for the product in the fields of leather and textile treatments, adhesives and sealants, plastic laminates, fire retardants, primers for wood and other non-ferrous materials.

## wherever resistant colours of highest quality are required

In the broad spectrum of world-known\*) FINNTITAN TiO<sub>2</sub> pigment grades every application finds a reliable solution: RR grades for maximum exterior durability

RD grades for universal and special applications

RF grades for plastics and colour concentrates

Anatase grades for paper and manmade fibers.

NB: In the grade designation

Number 2 denotes superior dispersion speed

Number 3 denotes superior properties in the most exacting industrial and automotive uses.

This is the trademark of Kemira Oy, a large, versatile Finnish company. Modern production techniques and investments in research and product development are the secret of Kemira's success on the international market.

VUORIKEMIA Malminkatu 30, Helsinki, Finland Agent in the U.K.: CORNELIUS CHEMICAL CO., LTD, Ibex House, Minories, London, EC3N 1HY

# Further investigation of the photo-induced oxidation of normal primary alcohols by anatase titanium dioxide

#### By M. A. Malati and N. J. Seager

Mid-Kent College of Higher and Further Education, Chatham ME5 9UQ, England

#### Summary

Irradiation of a suspension of anatase titanium dioxide in normal primary aliphatic alcohols with ultraviolet rays in a nitrogen atmosphere, led to the formation of  $Ti^{3+}$  ions and the corresponding aldehyde in solution. The yield of  $Ti^{3+}$  ions from a suspension in n-butanol increased linearly with irradiation time but the increase in the yield was not linear with the increase in the concentration of the pigment. The yield of  $Ti^{3+}$  ions was not significantly affected by the thickness of the layer irradiated or

#### Keywords

Processes and methods primarily associated with

analysis, measurement or testing

photo-oxidation

Miscellaneous terms

UV light

by the concentration of ethanol in alcohol/water mixtures. There was a drop in the yield with an increase in the alcohol chain length. Measurement of the absorbance at 278nm of the distillate, obtained from the irradiated reaction mixture, was used to estimate the yield of butyraldehyde, using a calibration plot of the absorbance of solutions of butyraldehyde in normal butanol. The yields obtained were similar when a suspension of either a commercial or a pure sample of TiO, was used.

Raw materials

prime pigments and dyes

anatase titanium dioxide rutile titanium dioxide

## Une étude supplémentaire de l'oxydation photo-amorcée des alcools primaires et normaux provoquée par le dioxyde de titane du type anatase

#### Résumé

L'irradiation ultra violette en l'atmosphère azotique d'une suspension de dioxyde de titane du type anatase dans les alcools aliphatiques primaires et normaux a pour résulte la formation des aldèhydes qui correspondent et également des ions Ti<sup>3+</sup>. Le rendement de ces ions à partir d'une suspension en n-butanol s'augmentait linéairement en fonction de la durée d'irradiation, mais le rendement ne s'augmentait pas de façon semblable en fonction de la concentration pigmentaire. Le rendement des ions Ti<sup>3+</sup> n'était pas influencé en grande partie, soit par l'épaisseur de la couche irradiée, soit par la concentration d'éthanol dans les mélanges d'alcool et d'eau. Le rendement diminue au fur et à mesure que la longueur de chaîne de l'alcool s'augmente. On s'est servi des mesures de l'absorbance à 278 nm du distillat en provenance du mélange distillé afin de déterminer le rendement d'aldéhyde butyrique en faisant appel à l'absorbance des solutions d'aldéhyde butyrique en n-butanol pour construire une courbe de calibration. Le rendement est semblable où l'on utilise une suspension du produit technique ou pur.

#### Eine weitere Untersuchung der photoinduzierten Oxydation der normalen Primäralkohole von Titandioxydanatas

#### Zusammenfassung

Die in einer Stickstoffatmosphäre ausgeführten Ultravioletbestrahlung einer Suspension von Titandioxydanatas in normalen Primäralkoholen brachte den entsprechenden Aldehyd und ebenfalls die Ti<sup>1</sup> Ionen hervor. Der Ertrag dieser iowen von einer N-Butanolsuspension stieg geradlinig mit der Bestrahlungszeit, aber die Ertragzunahme zeigte sich mit der Pigmentkonzentrationssteigerung nicht geradlinig. Der Ertrag der Ti<sup>1</sup> Ionen wurde weder von der Dicke der bestrahlten

#### Introduction

Refs, 1-3

The photo-induced oxidation of normal primary alcohols in which anatase TiO<sub>2</sub> is suspended has been previously Schicht noch von der Äthanolkonzentration in den Alkohol-Wasser Gemengen wirklich beeinflusst. Eine Vergrösserung der Alkoholkettenlänge verursachte eine Ertragverminderung. Die Messung des Absorptionskraft an 278 nm von dem bestrahlten Reaktionsmischung erhalteden Destillate wurde angewandt, um der N-Butyaldehydertrag mittels einer Eichkurve der Absorptionskraft der in N-Butanol aufgelösten Butyraldehydes zu bestimmen.

reported<sup>1</sup>. The butyraldehyde produced from n-butanol has been determined by gas chromatography, whereas  $Ti^{3+}$  ions simultaneously formed have been determined titrimetrically<sup>1</sup>. Cundall *et al.*<sup>2</sup> have studied the photo-oxidation of propan-2-ol in which rutile or anatase  $TiO_2$  have been suspended. The rate of production of acetone,

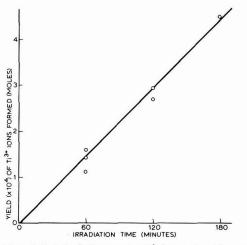


Figure 1. Variation in the amount of Ti<sup>3+</sup> ions produced from nbutanol/P25 suspensions with irradiation time

determined by gas chromatography, was found to increase with an increase in the powder weight and with an increase in the oxygen pressure<sup>2</sup>. The photo-reactions on oxide surfaces have been recently reviewed by Bickley<sup>3</sup>.

In the present investigation, the earlier work<sup>1</sup> on the photo-induced oxidation of normal primary alcohols has been extended to include the effects of the irradiation time, weight of powder, chain length of the alcohol; the concentration of butyraldehyde produced was determined by UV spectrophotometry. The proton magnetic resonance spectrum of the distillate from the reaction products has also been determined.

#### Experimental

#### Refs, 1, 4-6

The well-characterised<sup>4</sup> pigment anatase P25 (Degussa, Frankfurt) was used as supplied  $(AI_2O_3 < 0.3 \text{ per cent},$  $SiO_{2} < 0.2$  per cent) unless otherwise stated. For comparison, an anatase sample CLDD/881A (BTP Tioxide Ltd, London) which had received no surface treatment was also used in the form supplied. Analytical and surface area data for the latter sample have been recently published<sup>5</sup>. A suspension of P25 in normal primary alcohol was magnetically stirred whilst being irradiated with the unfiltered radiation from a Hanovia 100 W medium pressure mercury lamp. The details of the irradiation procedure and analysis of Ti3+ ions formed in solution have been published earlier'. For the determination of butyraldehyde formed on irradiating n-butanol, the filtrate from the reaction mixture was fractionally distilled using a 12" column. The first batch of the distillate was weighed and an aliquot was heated with dilute NaOH solution on a water bath for 40 minutes to suppress the possible formation of hemiacetal. The absorbance of the solution was measured<sup>6</sup> at 278 nm using a 10 mm cell in a Coleman 55 spectrophotometer. AR n-butanol, which had been treated in an identical way to the test solution, except for irradiation, was used as a blank. The percentage of butyraldehyde produced was obtained by interpolation

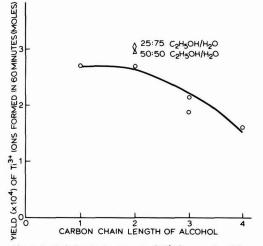


Figure 2. Variation in the amount of Ti<sup>3+</sup> ions produced from P25 suspensions in alcohols with the number of carbon atoms in the normal alcohol

from a linear calibration graph of standard solutions of AR butyraldehyde in AR butanol. The spectra of the standard or the test solutions showed that they were stable for at least a week.

The proton magnetic resonance spectrum of the distillate was recorded on a Hitachi Perkin Elmer spectrometer R-24 B, using tetramethyl silane as a reference. The bands on either side of the butanol doublet at 3.55-3.63 ppm were recorded again after increasing the amplitude 10 fold.

#### **Results and discussion**

#### Refs, 1, 2

Figure 1 demonstrates the linear variation with time of the concentration of  $Ti^{3+}$  ions produced by irradiating P25 suspended in n-butanol (1 per cent w/v). A similar linear variation has been reported<sup>2</sup> for the photo-oxidation of propan-2-ol by rutile TiO<sub>2</sub>. Since the amount of  $Ti^{3+}$  ions produced in 60 minutes was accurately measurable, this irradiation time was used for most subsequent runs.

Figure 2 depicts the amount of  $Ti^{3+}$  ions produced when different normal primary alcohols were irradiated with P25 for 60 minutes. The yield of  $Ti^{3+}$  ions decreased to some extent as the carbon chain length increased.

The faint blue/grey colour of the irradiated anatase was found to revert to white when exposed to air for some days, suggesting that the blue colour may be ascribed to the partially reduced anatase surface which was slowly reoxidised in air.

The effect of the concentration of the pigment P25 on the yield of Ti<sup>3+</sup> ions is shown in Figure 3, which indicates a non-linear increase in the yield with increasing pigment concentration. A similar plateau, reported by Cundall *et al.*<sup>2</sup>, has been explained by the complete utilisation of the radiation entering the reaction vessel by the concentrated suspensions.

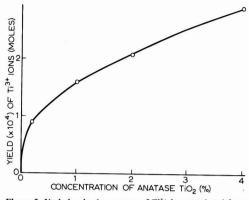


Figure 3. Variation in the amount of Ti<sup>3+</sup> ions produced from P25 suspensions in n-butanol with pigment concentration

When a narrower reaction vessel was used (reducing the thickness of the suspension to 4 mm), the yields of Ti<sup>3+</sup> ions produced in 60 minutes (1.6 and  $1.8 \times 10^{-4}$  mol) were similar to the corresponding yields depicted in Figure 1. This indicates that the reaction was most efficient in the suspension layer close to the lamp.

Figure 2 also shows that the yield of Ti<sup>3+</sup> ions produced by irradiating a suspension of P25 in C<sub>2</sub>H<sub>2</sub>OH/H<sub>2</sub>O by interfactors for 60 minutes, did not vary substantially with the alcohol concentration. The yield of  $Ti^{3+}$  ions produced from a suspension of P25 in n-butanol, previously treated with phosphoric acid, was about 10<sup>-5</sup> mol in 60 minutes. This drastic reduction in the yield, compared to the yield obtained from untreated anatase P25 (Figure 1), suggests that treatment with  $H_3PO_4$  possibly resulted in the adsorption of phosphate ions at the Ti<sup>4+</sup> surface sites rendering them much less accessible to attack by electrons produced on irradiating the anatase surface.

When suspensions of P25 or of CLDD/881A in nbutanol were irradiated for 180 minutes, the yields of

butyraldehyde were 3.3 and  $3.9 \times 10^{-4}$  mol respectively. These were calculated by interpolation from the calibration plot.

The proton magnetic resonance spectrum of the distillate from the anatase/n-butanol reaction, exhibited a peak at 4.3 ppm. This possibly indicates the hemiacetal assumed to be formed<sup>1</sup> according to:

 $C_3H_7CHO + C_4H_9OH \rightarrow C_3H_7CH(OH)OC_4H_9$  (1)

The proposed mechanism of the reaction<sup>1</sup> is:

IV→	e-	+	⊕	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	(2)	)
(i <sup>4+</sup> +	e		÷₿	Гi	3+																									(3	)

$$2OH + RCH_{2}OH \longrightarrow RCHO + 2H_{2}O \dots (5)$$

Since the release of Ti<sup>3+</sup> ions to the solution seems to be incomplete, and since the aldehyde and/or the hemiacetal may be adsorbed by the oxide, no stoichiometric relation between the two products is expected.

#### Acknowledgement

Thanks are due to Dr J. I. Hoppé for his interest and to Dr B. R. T. Keene for measuring the proton magnetic resonance spectrum and for helpful discussion.

Received 4 February 1981

#### References

279

ŀ

- 1. Buss, A. D., Malati, M. A. and Atkinson, R., JOCCA, 1976, 59. 369.
- 2. Cundall, R. B., Rudham, R. and Salim, M., J. Chem. Soc. Faraday I, 1976, 72, 1642.
   Bickley, R. I., in "Chemical Physics of Solids and Their Sur-
- faces", Vol. 7, p.118, The Chemical Society, London, 1978.
- Boehm, H. P., Disc. Faraday Soc., 1971, 52, 264. 5. Malati, M. A. and Smith, A., Powder Technol., 1979, 22,
- 6. Oshima, H., Bull. Chem. Soc. Japan, 1961, 54, 846.

## **Estimation of shellac**

#### By N. Prasad and B. B. Khanna

Chemistry Division, Indian Lac Research Institute, Namkum, Ranchi - 834 010, India

#### Summary

The estimation of shellac in the presence of other resins is possible by estimating the amount of water-soluble aldehydic acids present in the lac resin, either by sodium sulfite addition or absorption in the visible region due to the 2.4-

#### Keywords

Types and classes of coatings and allied products

shellac

Raw materials for coatings

binders (resins, etc.)

natural resin

#### La détermination de gomme laque

#### Résumé

On peut effectuer la détermination de gomme laque en présence d'autres résines en faisant la détermination des acides aldéhydiques solubles à l'eau de la résine de gomme laque, soit par l'addition de sulfite de soude, soit par l'absorption du spectre visible

#### **Die Bestimmung von Shellack**

#### Zusammenfassung

Es ist möglich die Bestimmung von Shellack in Anwesenheit der anderen Harze bei der Bestimmung von den wasserlöslichen Aldehydischharzsäuren mittels entweder eines Natriunsulfitezusatzes oder der sichtbaren Absorption vom 2:4

#### Introduction

#### Refs, 1-16

The identification and estimation of shellac, like that of any other natural resin is a difficult task. The problem becomes all the more difficult when it is present in a mixture. After the development of a successful method for the identification of shellac', it was desirable to find a suitable method for the estimation of shellac in a mixture with other resins, natural or synthetic.

A review of the literature shows that not much work has been done in this respect. Bhattacharya<sup>2</sup> recommended a procedure which was claimed to indicate the approximate amount of lac present in a mixture with other resins. The method was based on the isolation of the zinc salt of shellolic acid, a constituent acid of shellac obtained by the alkaline hydrolysis of the resin mixture. Vollmann<sup>3</sup> laid stress on the isolation of aleuritic acid from shellac and its mixtures with other natural resins. The preparation of the zinc salt of shellolic acid or isolation of aleuritic acid, are very dinitrophenylhydrazine derivative. Various mixtures give values in direct proportion to the amount of shellac present in them. The methods developed are simple and rapid.

Supplies and other materials primarily associated with analysis, measurement or testing

analytical reagent

grâce au dérivé de 2:4 DNPH. Les divers mélanges donnent des valeurs qui sont directement proportionnelles à la teneur en gomme laque des mélanges. Les méthodes perfectionnées sont faciles et rapides à faire.

DNPH Derivate auszuführen. Verschiedene Mischungen geben Werte, die in gerade Verhältnis zu dem Shellackgehalt stehen. Die entwickelten Methoden zeigen sich leicht und schnell.

laborious and time consuming. Moreover, when the percentage of shellac in the mixture is low, it becomes very difficult to use their methods. It will be thus seen that there is no reliable method for estimating shellac in a mixture with other resins. An attempt has therefore been made to develop a rapid and simple method for its estimation.

As regards the chemistry of lac resin, it has been shown by several workers<sup>4.8</sup> that the resin is composed of a number of hydroxy aliphatic and sesquiterpenic acids. The major acids present in the pure resins<sup>9,10</sup> are aleuritic (I), jalaric (II) and lacci-jalaric acids (III) which have the structures shown opposite.

Aleuritic acid has a characteristic vicinal hydroxyl whilst both jalaric and lacci-jalaric acids have aldehydic groups. Methods are available for the estimation of aleuritic acid in lac resin by utilising the oxidation of its vicinal hydroxyl either with periodic acid<sup>11</sup> or by lead tetra-acetate<sup>12</sup>. Similarly, the estimation of aldehydic acids (both jalaric and lacci-jalaric acids) in lac resin has been achieved by sodium sulfite addition<sup>13,15</sup> or the 2,4dinitrophenylhydrazine (2,4-DNPH) method<sup>14</sup>. The other

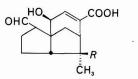
#### 1981(6) ESTIMATION OF SHELLAC

natural resins used in the present study for preparing mixtures with shellac were rosin, damar, gamboge, kauri, pontianac and dragon's blood. Most of these resins have measurable acid and hydroxyl values suggesting that they contain carboxyl and hydroxyl groups. As reported<sup>1</sup>, these natural resins, like lac resin, also give positive tests of silver mirror formation with Tollen's reagent. At first, it was thought that the estimation of vicinal hydroxyl or aldehydic acids might be directly related to the amount of shellac present in the mixture.

It has already been reported<sup>7,8,11</sup> that with estimation by means of periodic acid oxidation, the value of the vicinaldihydroxy content before hydrolysis (11-13 per cent) is nearly one-third of that found after hydrolysis (32-35 per cent) in the case of lac resin and its ether fractions. The other natural resins used in the present study also contain the vicinal-dihydroxy system as they give a positive test<sup>1</sup> with periodic acid oxidation. Thus, it does not appear feasible to estimate the amount of lac in various mixtures with other natural resins in terms of aleuritic acid content utilising the periodic acid oxidation method.

The second choice was to make the estimation by reaction of the aldehydic group of lac resin. It has been established that aldehydic (jalaric/lacci-jalaric) and other terpenic acids present in lac are highly water-soluble, whilst the aliphatic constituents aleuritic, butotic, etc. are water insoluble. The constituent acids of shellac are liberated on hydrolysis with an alkali followed by decomposition with a mineral acid. The aqueous portion which separates out contains mainly terpenic constituents. In this aqueous portion, jalaric and lacci-jalaric acids can easily be detected by reaction with 2,4-DNPH or with Tollen's reagent. The other natural resins used in the present study were also subjected to the above hydrolysis and the aqueous portion recovered from each after decomposition with a mineral acid was not found to give a positive test for aldehyde with Tollen's reagent. An attempt was therefore made to estimate the aldehydic acid from the aqueous portion obtained as above, utilising sodium sulfite addition<sup>13,15</sup> and absorption<sup>16</sup> in the visible region (using an alkaline solution of the 2,4-DNPH derivative).

OH | HO•CH<sub>2</sub>•(CH<sub>2</sub>)<sub>5</sub>•CH•CH•(CH<sub>2</sub>)<sub>7</sub>COOH . . . . . . . . (1) | OH



$$R = CH_2OH \dots (II)$$

#### (a) Sodium sulfite method 13,15

#### Refs, 13,15

Nearly 1 g of shellac (finely powdered) accurately weighed was taken and hydrolysed with 0.5 N aqueous sodium hydroxide (10 ml) by refluxing for 5 hours at water bath temperature. The resulting hydrolysed product after cooling, was decomposed with dilute sulfuric acid with thorough stirring to make it just acidic to congo red paper. The aqueous portion was separated by filtration in a measuring flask (100 ml) and the residue repeatedly washed with distilled water, all the washings were collected in the measuring flask and the volume was finally made up to the mark with distilled water. Thereafter, 5 ml of the solution was taken and to it 20 ml of standard sodium sulfite (0.8 N) and 5 ml of standard sulfuric acid (0.1 N) were added. After thorough mixing, it was allowed to stand in the dark for 30 minutes at room temperature and the excess of acid was titrated with standard alkali (0.1 N), using thymolphthalein as internal indicator. A blank was also run side by side.

The estimation of aldehydic acids was made on the basis of the following calculation:

percentage of aldehydic acids	$(A + B - C) \times N$ of alkali $\times$ (EW of jalaric acid)* $\times$ 100	
	 W × 100	

Where:

- A = ml of standard alkali solution needed to neutralise the free acidity
- B = ml of standard alkali solution needed to titrate the blank
- C = ml standard alkali solution needed to titrate the sample after reaction

W = weight of sample taken

EW of jalaric acid = 280.

Different varieties of shellac (palas, kusum and ber) (fresh and old) were taken and subjected to the above treatment for the estimation of aldehydic acids where an average value of 30 per cent was obtained.

The other natural resins were also subjected to the above hydrolysis and similar estimations were made, but none of them indicated the presence of water-soluble aldehydic acids. Mixtures were prepared using different proportions of lac and other natural resins and the above method was followed to estimate the percentage of aldehydic acids where various mixtures gave values in direct proportion to the amount of shellac present in them.

#### (b) Spectroscopic method in the visible region <sup>16</sup>

The 2,4-DNPH method<sup>16</sup>, which depends on the absorption at 480 nm using an alkaline solution of 2,4-DNPH, could be easily standardised in terms of jalaric acid and hence was adopted for the estimation of aldehydic acid units in lac resin.

The addition of alkali to a 2,4-DNPH solution produces an intense wine-red colour, the absorption maximum ( $\lambda$ max 480 nm) and specific intensity ( $\epsilon$  480 = 2.72 × 10<sup>4</sup>)

\*Since the percentage of aldehydic acids other than jalaric acid is extremely low in the resin, the latter has been taken.

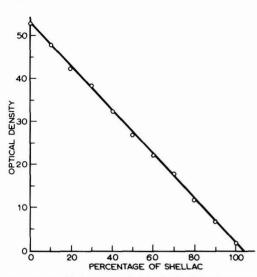


Figure 1. Relation between optical density (at 480 nm) and the percentage of shellac

have been demonstrated<sup>16</sup> to be nearly independent of the structure of the carbonyl compound. However, it was established experimentally<sup>17</sup> that an alkaline solution of jalaric acid 2,4-DNPH has  $\lambda$  max 480 nm,  $\varepsilon = 1.21 \times 10^4$ and these values were employed for estimating jalaric/lacci-jalaric acid residues in lac resin.

The water-soluble aldehydic acids were obtained from various shellac samples as described in method (a). Exactly 5 ml of aqueous solution was measured into a conical flask and to it 25 ml of a aldehyde free methanol, 1 ml of 2,4-DNPH solution (saturated solution of 2,4-DNPH in aldehyde free methanol) and one drop of conc. hydrochloric acid were added. The mixture was heated for 3 hours at 50-60°C. After cooling, 5 ml of potassium hydroxide solution (prepared by dissolving AR KOH (10 g) in water (20 ml) and diluting with carbonyl free methanol to a total volume of 100 ml) was added to it, whereupon a wine-red solution was obtained. A blank was also run side by side and  $\lambda$  max for these solutions were obtained. The average value of specific intensity for different samples of shellac at  $\lambda \max 480 \text{ nm}$  was calculated and found to be  $\epsilon = 1.92 \times 10^4$ ). On further calculation, an average value of 32 per cent aldehydic acids was obtained.

The same method was also applied to other natural resins used in the present study but none of them indicated the presence of any water-soluble aldehydic acids. The method was also applied to various mixtures of lac and other natural resins and the results obtained are shown in Figure 1. The curve represents the average values obtained with different mixtures of lac and natural resins.

#### Discussion

Ref. 15

no significant difference in percentage of aldehydic acids among fresh or old and different varieties of shellac, which confirms the earlier findings15. As the percentage of aldehydic acids is directly proportional to be amount of shellac present in the mixture with other natural resins, this can serve as a direct method for estimating shellac in the presence of other natural resins.

Method (b) can also be used for estimating shellac in a mixture with natural resins. As is obvious from Figure 1, there is a direct relationship between optical density (at 480 nm) and the percentage of lac present in the mixture, the optical density decreasing with increase in the percentage of lac in the mixture. Using the methods described, shellac concentration as low as 5 per cent could be estimated in a mixture.

The methods (a and b) discussed above were also applied to mixtures of shellac with some synthetic resins such as urea-formaldehyde, melamine-formaldehyde and phenol-formaldehyde. As these resins also gave positive values for water-soluble aldehydic acids, it is not feasible to estimate shellac in mixtures with synthetic resins containing aldehydic functions by the methods discussed above. The methods, however, hold good for mixtures of shellac with synthetic resins not containing aldehydic functions.

#### Acknowledgement

The authors are grateful to Dr T. P. S. Teotia, director and Sri S. Kumar, head of the Division of Chemistry for their interest. The technical assistance given by Sri T. K. Saha and Smt. P. Devi is also acknowledged.

[Received 27 January 1981

#### References

- Prasad, R. and Sengupta, S. C., JOCCA, 1978, 61, 49. 1.
- Bhattacharya, R., London Shellac Res. Bur., 1935, Tech. 2. Paper No. 2.
- 3.
- Vollmann, H., JOCCA, 1957, 40, 175. Christie, W. W., Gunstone, F. D. and Prentice, H. G., J. 4. Chem. Soc., 1963, 5768.
- Chem. Soc., 1905, 5105.
  Khurana, R. G., Singh, A. N., Upadhye, A. B., Mhaskar,
  W. V. and Sukh Dev., *Tetrahedron*, 1970, 26, 4167.
  Chatterjea, J. N., Sengupta, S. C., Misra, G. S. and
  Agarwal, S. C., *Indian J. Chem.*, 1976, 14 B (9), 719.
  Sengupta, S. C., *Ph.D. Thesis*, Ranchi University, India, 1070
- 6.
- 7. 1970.
- Prasad, N., Ph.D. Thesis, Ranchi University, India, 1978.
- 9. Singh, A. N., Upahye, A. B., Mhaskar, V. V. and Sukh Dev, Tetrahedron, 1974, 30, 3689.
- Singh, A. N., Upadhye, A. B., Mhaskar, V. V. and Sukh Dev, *Tetrahedron*, 1974, **30**, 867.
   Sengupta, S. C., J. Sci. Indust. Res., 1959, **18 A**, 221.
- 12. Bhatt, H. A. and Kamath, N. R., Curr. Sci., 1949, 18, 331. 13. Sengupta, S. C. and Tripathi, S. K. M., J. Sci. Indust. Res.,
- 1959, 18 B, 535.
- Lappin, G. R. and Clark, L. C., Anal Chem., 1951, 23, 541. 14
- 15. Sengupta, S. C., Agarwal, S. C. and Prasad, N., JOCCA, 1979, 62, 85.
- 16. Lappin, G. R. and Clark, L. C., Anal Chem., 1953, 25, 649. 17. Wadia, M. S., Khurana, R. G., Mhaskar, V. V. and Sukh Dev, Tetrahedron, 1969, 25, 3841.

The values obtained by method (a) revealed that there was

All correspondence should be addressed to: Mr D. S. Newton, Honorary Editor, OCCA, Priory House, 967 Harrow Road, Wembley, Middlesex, HAO 2SF, England.

## "Effect of pigmentation level on the efficiency of triple roll milling", JOCCA, 1980, 63 (11), 438-445

Sir – Dr Carr's letters (JOCCA, 1981, January and April) called for a definition of "wetting". It was the phrase, "the pigment appeared to be well wetted out" in the original paper on triple roll miling (JOCCA, 1980, November) that roused me! Dr Carr did not provide a definition, but if one were needed – and I don't regard wetting as a red herring – I'd be content with Patton's definition in his "Paint Flow and Pigment Dispersion" (Interscience, 1964) on p. 217. One could thus assume a state of perfect wetting (and dispersion) when all the pigment has been separated into primary particles which are completely wetted. Such a state, although probably impossible to attain, is nevertheless the one to aim for in high quality dispersions of enamels, inks etc.

Dr Carr asks whether I agree with the findings. Well, bluntly no! Triple roll (or sand) milling results mean little unless the premixing has been efficiently carried out in a high shear intensive mixer starting with as high a pigmentation as possible. With progressive dispersion and wetting more liquid has to be added to allow adequate flow. This could be illustrative of the Merkle/Herbst phenomenon - quoted by Mr Scott (JOCCA, 1981, April) - because unless there is sufficient liquid, to enable flow to occur, there will be insufficient liquid to be adequately distributed between the available particles. Of course the addition of more liquid to the mix eventually reduces the efficiency of mixing/milling/wetting/dispersion because the pigment concentration is reduced. Therefore, the stage is eventually reached when the pigment paste must be transferred to another mill (sand or triple) in which small portions of the paste are subjected to more intensive milling (or refining). Thus the premixing and milling are really two essential components of one operation and when I'm confronted with the statement "well wetted out by hand" - well!

I trust Mr Scott will let me enter the fray with respect to Hegman gauges. I doubt whether any triple roll mill user would think that the Hegman gauge refers to anything but the size of the largest cluster of particles in the product. The gloss and colour are the resultant of the size, distribution and composition of *all* the clusters.

Finally, may I disagree once again with Dr Carr! By all means let us have a project on dispersion in all its aspects – but please not by an independent body with no axe to "grind" (the right word, of course, to use!) It would be far better for all interested parties to sharpen their axes and wade in!

Yours faithfully,
I. Berg
Ū.
12 April 1981

#### **Dr Carr Comments**

1981(6)

Sir – Mr Berg again raises the question of wetting. In physics text books, the ability of a liquid to wet a fine



powder, which is heavier than it, is determined by its surface tension (liquid/air) and its contact angle.

Organic pigments and carbon blacks are notoriously difficult to wet out with water and tend to float on the surface. Similar problems arise with many dyestuffs even though they are soluble in water.

The addition of a wetting agent will reduce the surface tension of the water and its contact angle with powders and therefore facilitate wetting of the powder, which will then sink under gravity. Grinding the powders in such solutions of wetting agents will not produce good dispersions unless the wetting agent is adsorbed on the surface of the powder, besides at the liquid/air interface. Many ionic wetting agents are adsorbed at the water/air interface and reduce the surface tension dramatically but have no affinity for the powder surface and hence provide no stabilising action so that milling is in vain.

On the other hand, the most effective ionic stabilising agents in water are strongly adsorbed at the powder surface and hence give a good stabilising action on milling, but they do not significantly reduce the surface tension of the water and have little or no wetting action. Consequently they have to be used in conjunction with a wetting agent or with a press cake where the pigment is already wetted out.

Non ionics will lower the surface tension of water and are also adsorbed on powder surfaces so that they have both a wetting and dispersing action.

In most non aqueous systems used in paints, the surface tension of the vehicle, whether oil or solvent, is usually low so that wetting of the pigment is not a problem. The mill is the dispersing agent and the system is stabilised by the adsorption of resin or surfactant molecules. If this adsorption is weak, the stabilisation is weak and the dispersion is poor.

That is why I think the emphasis on wetting is misleading; it is adsorption of long chain molecules onto the surface of the pigment that is the dominant factor in stabilising dispersions.

With regard to a project on dispersion, I suggest Mr Berg's letter itself shows the need for an independent approach, he has many years practical experience in the use of paint making machinery and, being a thinking man, has his own views and theories of what is happening. However, he can produce no dispersion, i.e. particle size measurements, to support them.

My former colleagues and I have measured particle sizes slowly and painstakingly in a limited number of systems and have found that dispersion levels are dependent on factors such as the mill and how it is used, methods of application and drying mechanisms and have come up with some surprising results.



Our work, however, has been limited to organic pigments in a small number of systems. Now that newer, very rapid techniques for measuring particle sizes are available, we feel that our work has done enough to show the need for a thorough investigation of the dispersions field.

Ideally, in my opinion, such work would need a team comprising a statistician (too keep down the number of experiments), a physicist to ensure the theoretical soundness and reliability of the particle size measurements and paint chemists familiar with formulations, grinding,



Water soluble polymers, developments since 1978

#### Yale L. Meltzer

Noyes Data Corporation, New Jersey, USA

#### pp. 608 inc. introduction and index, Price \$54

As with all volumes in this series the developments in water soluble polymers are covered by reference to patent literature. 305 US patents published between 1978 and



## lrish

#### Get the best out of your paint

The fourth meeting of the 1980/81 programme was held at the Clarence Hotel, Dublin on Friday, 23 January.

This Meeting was a departure from the usual lecture, and consisted of an open forum with the theme "Get the best out of your paint". application and drying mechanisms and able to evaluate the resultant films.

The team should be familiar with both organic and inorganic pigments, and should not be beholden to any one pigment, resin, solvent or mill manufacturer. Very few research teams can be mustered along these lines outside the Paint Research Association and it would seem to me to be an ideal project for them, and would be well worth sponsoring by all branches of the paint industry.

I would like to repeat my thanks to Mr Berg for his continued interest and his forthright views.

> Yours faithfully, W. Carr

31 Lindow Fold Drive, Wilmslow, Cheshire SK96DT

12 May 1981

Further information on any of the publications reviewed may be obtained by circling the appropriate *Reader Enquiry Service* number on the form at the back of the *Journal*. Enquiries will be forwarded to the publisher.

1980 are described in sufficient detail to assess their importance to an interested researcher.

The book begins with a market survey in which the major polymers are identified and in some cases, capacities and breakdown by application are described.

One useful aspect of this type of publication is that it is possible to identify the areas of greatest research effort by the number of patents published, and on this criterion it is interesting to note the amount of effort still being expended on natural products such as gelatines, starches and natural gums.

This is, of course, a book for the reference library, where it should prove a useful addition.

Reader Enquiry Service No. 21

D.S. Newton

For information on membership of OCCA, enquiries should be sent to the Association's offices, see front cover for address.

A panel of three recognised authorities on paint and painting presented short papers, which were followed by discussion in open forum.

The panel members were:

Mr R. Simon	-	The Institute for Industrial Research and Standards
Mr M. O'Callaghan	-	Donald MacPherson & Co. (Ireland) Ltd
Mr J. Bastable	-	National Association Master Painters and Decorators of Ireland

The following were some of the many interesting points made:

Mr Bastable felt that the painters were now often confused by the proliferation of new products with various claims and often found it difficult to differentiate between different brands. He suggested that the paint industry should keep the consumer updated on modern paint technology and suggested a liaison committee between OCCA, the Irish Paint Manufacturers' Federation, the National Association Master Painters and Decorators, and the Institute for Industrial Research and Standards, to promote this.

Mr Simon stressed that wet blasting would be very useful in the future in achieving chemical cleanliness and cleaning a variety of substrates including steel, masonry and wood. Mr Simon also felt that there should be more awareness of the use of curing membranes in concrete, which act as a physical barrier to the adhesion of paint, and methods to facilitate the detection of such substances.

A most successful open forum followed, and from the response, it would seem that a further meeting of this nature should be considered.

P. McCrudden

## London

## Application of colour

A joint one day symposium with the London Region of the Society of Dyers and Colourists was held in association with Thames Polytechnic on 18 March 1981. A total of six papers were presented to an audience of 35, covering a range of applications of colouring materials and problems associated with the display and measurement of colour.

Mr D. C. Mason, ICI Paints Division presented the first paper entitled "Colour in decoration". In his paper, Mr Mason showed how the imaginative use of colour could contribute a great deal to brightening up our somewhat dingy environment. In particular he stressed how the public's perception of their environment could be enhanced by the bold use of colour in both new architecture and older buildings, particularly in the work place.

In his paper, Mr M. Taylor of Hainsch Colour International described the processes involved in the manufacture of colour swatches and pattern cards. Whilst much of the work was straightforward special techniques had to be adopted in certain situations. Particular problems highlighted were the presentation of displayed patterns of woodstains and textured finishes.

The development of colour difference measurement equations was the subject of Mr K. McLaren's paper (Instrument Colour Systems Ltd). Using practical examples from the field of textile dyeing he demonstrated how derived equations could be used with colour measuring instruments to improve the accuracy of quality control operations.

Mr A. C. Palmer, Williams Ltd presented a paper on the colouring of foodstuffs. The importance of colour both to the manufacturer and the consumer of food products was discussed. Whilst many naturally occuring pigments and dyes were still used by the food industry, increasing importance was being given to synthetic dyes and laked pigments. The use of dyestuffs was limited by their being



water soluble only; lakes could be used in other media particularly oils and fats and were thus used extensively in confectionery and convenience foods.

Mr J. Todd of Ciba Geigy, Plastics and Additives described how colours for plastics had followed the development in the type and nature of the polymers requiring colourants. The application and the properties of the plastic, dispersion and stabilisation determined the selection of the appropriate pigments for a particular polymer system.

In the final paper of the symposium Mr I. Hains, Ault and Wiborg Paints provided a paintmaker's view of instrumental colour measurement. In describing his own involvement in vehicle refinishing paints, Mr Hains indicated the value of computer controlled colour measurement and pigment selection facilities to his industry. For all its value the instrumental techniques still needed to be balanced with skilled colour matchers for factory batches.

A. J. Newbould

## West Riding

## **Colour systems**

A lecture meeting of the West Riding Section was held at the Mansion Hotel, Leeds, on 3 March 1981.

Mr G. Pakvis of Tenneco Colortrend BV, gave a presentation on the various colour tinting systems available from his company.

Mr Pakvis introduced his talk by giving a detailed review of the size of the European paint market. It was said that "in 1977, 50 per cent of paint sold through retail outlets in Europe was white. Of the remainder, 20 per cent was tinted through the use of a colour system".

The speaker suggested that the growth in the use of colour systems was due to the European paint market becoming more sophisticated. The paint manufacturer and retailer are beginning to recognise the cost saving possible through a reduced inventory.

Mr Pakvis illustrated, with numerous coloured slides, the many systems available through his company, the service provided to meet the demands of individual customers and also the colour preferences of different countries.

Although the talk was somewhat commercially orientated, Mr Pakvis did give some technical details of Tenneco's colour systems. The systems were said to be formulated in such a way that colour consistency, paint/system compatibility and paint scrub resistance were



maximised. Whilst the effects on paint viscosity, hardness, drying time and scrub resistance were minimised.

After a very searching and enthusiastic question period, the vote of thanks was given by Mr Eric Bishop.

D. V. Maltman

## Manchester

## Wood priming paints

The final student lecture of the 1980/81 programme was delivered before 30 members and guests at Manchester Polytechnic, All Saints on 18 February, 1981 by Frank Redman, Vice Chairman and his colleague Wilf Phillips. Both employed by Crown Paints Ltd, Darwen, in the laboratories.

The lecture was divided into three parts and can be reported in the following summarised form:

- 1. Wood substrate by W. Phillips
- 2. Solvent borne paints by F. Redman
- 3. Water borne paints

Both lecturers used many slides to illustrate their respective lectures.

Wood:

dimensionally unsuitable/variable porosity attacked by insects/rot natural product, variation in quality due to geographical location subject to lack of seasoning formulations required for problem wood applied by brush hands not decorator

On a topical digression, Wilf Phillips defined timber as wood of considerable dimensions. In the USA timber is known as lumber.

Timber sources: hardwood – deciduous trees softwood – coniferous trees

The variability of wood is associated with 3 basic sections, i.e.

- (i) springwood large pores sapwood
- summerwood small pores heartwood
- (ii) growth rings
- (iii) flat grain/edge grain/end grain

moisture content - resin content

## Solvent based primers by F. Redman

On a historical note, before 1914 the majority of timber grew slowly and thus had a close grain with low absorbancy. Lead based primers were widely used until environmentalists objected. This lead to the decline in lead based primers, generally lower performance of the alternative materials used and the result was criticism of the paint industry in general. Other factors include on-site storage, building practices, water ingress – high movement potentials.

The lecturer described the PRA Timber Porosity Test which is based on the absorption time/pattern of dyed isopropanol.

He stressed the point that the paint industry had been subjected to and accepted the pressures from the automatal joinery manufacturers who required low cost primers, having as their main criteria, good blocking resistance. The main types of timber used are Baltic Red Cedar and Scots Pine.

Frank Redman then discussed formulation development in detail and made specific reference to matching the performance of lead based primers, e.g. BS 2521:1966, by emphasising the importance of the following properties:

- Formulation opacifying pigment, extender, oils long oil alkyd, organo metal driers (not lead) and mineral spirits
- 2. P/B ratio
- 3. Exposure natural and accelerated BS 5358 panels used
- 4. PVC variable between 30-49% dependant on wood type etc.
- Extender choice very important use of mica to reduce permeability. Use of low carbonate type talcs
- 6. Preservatives
- Aluminium pigmentation for resin/knot sealing but problems with intercoat adhesion
- Exposure tests results include reference to:
   (a) quality of wood
  - (b) cracking detected by ×10 magnification
  - (c) micro cracking detected by  $\times 10 \times 100$  magnification
  - (d) incipient cracking detected by  $\times 100 \times 200$  magnification

## Water borne wood primers by W. Phillips and F. Redman

Whilst this lecture was of a joint venture there was an element (friendly) of water versus oil in the content and subsequent discourse.

W. Phillips commenced by showing slides (electron micrographs) which illustrated relative sizes of the polymer and extender particles.

With regard to polymer choice Mr Phillips obviously favoured acrylic and he claimed that the adhesion of the new acrylic latex coatings modified to improve wet adhesion were the coatings of the present and future, and could only be challenged by the alkyd modified latex coatings. There is a relevant BS specification, No. 5082, for wood primers and the lecturer, who has served on the relevant BS committee, claimed the following parameters were relevant:

- 1. Need to replace BS 2521
- 2. A quick drying, non-toxic, non-flammable product required
- 3. Need to define an adequate level of performance, especially durability

Specific test methods included the following:

1. Blister box test GLC versus BS 5082 Slides illustrating the apparatus were shown, Wilf Phillips made reference to two polymers used, VA/ethylene copolymers and styrene acrylics.

2. Wet adhesion versus durability

NB Wet adhesion and polymer flexibility very important Formulation details discussed were:

- (a) lightly coated titanium dioxide
- (b) large particle size extenders plus lamella types, lowest OĂ
- (c) binder as previously described
- (d) dispersants low water solubility/foaming
- (e) coalescents not completely water soluble, resistant to hydrolysis
- (f) thickener good flow except on sharp edges maximum water resistance minimum support for mould growth

Biocides: in-can preservation film protection - moulds and algae wood protection - blue stain rot

The 3 lectures were followed by a lively discussion period which included reference to the increase in stain usage, permeability, the UK end-users' obsession with gloss, and future trends including planned reaction between the polymer and the cellulose fibres in wood. Geoff Flood, the Student Activities Officer, concluded the excellent 2 hour meeting with a vote of thanks, the response to which indicated both the quality of the lecture and the general excellence of student lectures in the Manchester Section: attributable in turn, to Geoff Flood, whose efforts now completed, will be travelling to pastures new

F. B. Windsor

## Trent Valley

## British Railways paint testing and specifications

The Trent Valley branch of the Midland's Section of OCCA held its fourth meeting of the current session at the Crest Motel, Littleover, Derby on the evening of Thursday 12 March 1981.

Dr Frank Zobel, head of the Surface Coatings



laboratory at British Rail, invoked David Bishop, Rudyard Kiplin's six good serving men and an eccentric, epideictic device, to explain to the expectant gathering of twenty-five enthusiastic members and guests, something of the historic development of paint testing methods since 1949, and the current views of British Rail on paint specifications. Since 1970, paint performance and long life coatings which can be easily maintained have been the goal of the Derby based team, who have enlisted both paint manufacturers and suppliers to these ends.

Dr Zobel confirmed that toxic pigments were being avoided, to help eliminate hazards during the removal of old paint films during repainting. Members present at the meeting recalled the recent paper in JOCCA on the classification of micaceous iron oxide by David Bishop, and Dr Zobel explained how they had discovered that only the well defined laminar varieties were desired by British Rail for use in their paint systems.

Dr Zobel went on to elaborate how rheological characteristics determined the optimum in application and sag resistance, especially in the use of high-build coatings.

Throughout his lecture, Dr Zobel made skilful use of several colour slides, some of which evoked fond memories of steam locomotives. So complete was his mastery of the subject, that Dr Zobel was well able to cope with the idiosyncractic slides, which often appeared to be inside-out and on more than one occasion upsidedown!

A lively question period followed and extended the lecture.

Frank Timmins rose to the occasion and proposed a sincere vote of thanks to Dr Zobel and his team for providing an entertaining evening.

The meeting dined on British Rail sandwiches and coffee before dispersing into what was left of the night.

J. R. Kitchen

Further information on any items mentioned below may be obtained by circling the appropriate Reader Enquiry Service number on the form at the back of the Journal. Enquiries will be forwarded to the organisation concerned.

#### Quality control investment by SRL

Synthetic Resins Ltd have completed a comprehensive redevelopment of quality control facilities at the company's Merseyside plant. The factory manufactures resins primarily used in surface coatings, reinforced plastics, abrasives, impregnated paper and the foundry industry.

Three new laboratories have been established to help ensure adherence to

1981(6)

quality and performance standards, particularly for SRL's range of environmentally sensitive products where legal standards on threshold limit values (TLV) apply.

Reader Enquiry Service No. 31

#### Ellis Jones manufacture azo pigments

Ellis Jones and Co. Ltd have taken over



the manufacture and sales of all azo pigments previously manufactured by CIL Gould Ltd. Reader Enquiry Service No. 32



### **Haeffner** expansion

As part of their continuing policy of expansion, H. Haeffner and Co. Ltd have announced the opening of their northern sales office in Congleton. The new office will serve mainly customers in the northern areas. At the same time, more warehousing in the Manchester area has been taken on with the intention of providing customers in the Midlands and the north with a faster and more efficient service, by offering ex stock deliveries of the full range of Haeffner products. *Reader Enquiry Service No. 33* 

### New premises for Norwegian Talc (UK) Ltd

Norwegian Talc (UK) Ltd has moved to larger premises, the new address is: 205 Cotton Exchange Building, Old Hall Street, Liverpool L3 9LA. Telephone (051-236 6435) and telex (627012) numbers remain the same.

The move has been precipitated by an expanding level of business and hence the need to increase the number of staff.

Mr A. R. Gadd has rejoined Norwegian Talc (UK) as general executive director after an absence of three years.

Reader Enquiry Service No. 34

## TBMA install advanced paint plant

TBMA (UK) Ltd, specialists in the development of complete process systems for industry, have produced an advanced paint manufacturing plant for Silver Paint and Lacquer Co. of Yorkshire.

The fully automatic system, designed and built in conjunction with Mastermix Engineering, encompasses the entire paint manufacturing process from base materials to finished product, ensuring increased quality and consistency through accurately controlled processing. The system also provides flexibility in paint formulation and a fourfold increase in production potential.

The sequence of operations is supervised by one man from a purposebuilt control console which incorporates a full mimic display and manual over-ride facilities.

Reader Enquiry Service No. 35

Arrangements have been completed for what is believed to be the first ever French denationalisation with the acquisition of Ripolin Limited UK (76 per cent owned by Le Ripolin) by Jacoa Limited.

Advised by Barclays Merchant Bank and Barclays Development Capital, Jacoa successfully tendered for the Le Ripolin 76 per cent holding in January 1981 and at the same time made a similar offer for the 24 per cent minority shareholding.

Jacoa Limited was formed in October 1980 by the executive main board directors of Ripolin Limited UK with the intention of making an offer for the Le Ripolin holding, which in turn is controlled by the French stated owned Cdf Chimie.

Reader Enquiry Service No. 36

## Bestobell join SPL

Silver Paint and Lacquer (Holdings) Ltd, manufacturers of Home Charm paints, acquired the paint and chemical division of Bestobell Ltd for a total cash consideration of  $\pounds 2.25$  million.

SPL, which is privately owned, has interests in wallpaper, maintenance chemicals and synthetic resins, together with its two decorative branded paints Home Charm and Deloria. The Bestobell division, which has similar interests in paint and maintenance chemicals, sells under the brand names of Carsons Sunway and Hadfields.

SPL's acquisition will strengthen the paint and chemical interests of both companies and will create a combined group with a turnover in excess of £35 million, employing in the region of 1,000 people.

The new group will be divided into two separate paint and chemical divisions; the paint division headed by the present SPL chairman, Leslie Silver, the chemical division by Donald Komrower. *Reader Enquiry Service No. 37* 



### **Amorphous silica**

Compounding Ingredients Limited of Manchester have now made available four grades of amorphous silica. By virtue of its inert properties, neutral pH and chemical/minerological composition it is an extremely versatile inert filler for use in surface coatings. It is also finding increased acceptance as a filler for polyurethane elastomers, silicone rubbers, epoxy compounds, thermoplastics and many other applications.

High purity and neutral pH make

amorphous silica virtually non-reactive with other chemical compounds, making it suitable for use in corrosion resistant coatings.

Reader Enquiry Service No. 38



The variable ratio Hydra-Cat

## New proportioning systems

Plural component materials of almost every type can be proportioned, mixed and applied with a new range of airpowered systems from Graco.

The Variable Ratio Hydra-Cat is available in ten models which between them cover mix ratios from 1:1 to 18:1 with output pressures of up to 180 bar and delivery volumes up to 15 litres a minute.

This broad selection provides a proportioner for materials such as polyurethanes, epoxies, silicones, polysulphides and polyesters, in the form of decorative and protective coatings, adhesives, sealants, casting and moulding materials and foams. It covers application by air spray, airless spray, extrusion or low-volume pour.

All ten models are based on a common frame, a choice of two air motors and a range of proportioning cylinders. Each model provides an infinitely-adjustable range between two specified mix ratio limits. Ratio changing is easy and can be done in minutes. Extra cylinders can be added for colourant injection or solvent addition and a ratio-check valve is provided to verify proportioning accuracy.

Apart from eliminating mix-ratio and pre-mixing errors, the Variable Ratio Hydra-Cat can significantly reduce waste from spillage and left-overs since material is mixed automatically on demand. Substantial time savings are possible too, since pre-mixing is unnecessary and the base materials can be pumped directly from their original supply container. *Reader Enguiry Service No. 39* 

## Solvent reclamation

A new solvent reclaiming machine, the Solvit, has been developed by Polyflow (Developments) Ltd. The Solvit has a capacity of 200 litres and an output of 20 to 30 litres per hour. Its main features are that the equipment is very simple to use as just one switch operates the whole plant and no cleaning or inhibitors are required.

A conventional 200 litre drum is placed in the machine and filled with the contaminated solvent. When reclamation has been completed the drum containing the waste solids is removed, thus avoiding any contact with toxic waste. Reader Enquiry Service No. 40

## New curing agent

A new polyamino amide curing agent, known as Epilink, has recently been added to the Epilink range supplied by Akzo Chemie.

The new product is claimed to have better colour than previous materials and excellent adhesion to non-ferrous metals. Reader Enquiry Service No. 41



The RB10 colour density monitor

### **Colour density monitor**

Sick Optic-Electronic Ltd has developed a colour density monitor which combines the precision of a laboratory instrument with the rugged construction essential for industrial production environments.

The RB10 system comprises an optical head and an electronic processing unit. The optical head operates on the modulated twin beam principle which totally eliminates the effects of fluctuating parameters such as temperature, voltage and ambient light. Evaluation of the signals from the optical head is performed by the electronic unit which incorporates a digital display of measured value, high and low alarm set points and has a 0-20 mA current output, enabling connection to an external chart recorder or data processor to be made.

The RB 10 will measure very small deviations in colour from a pre-set reference value, and is in use in a wide range of industries. Reader Enquiry Service No. 42



EIL's new pH meter

## New pH meters from EIL

EIL Analytical Instruments have introduced two laboratory pH meters. The new instruments are mains operated with digital readout (LED), featuring illuminated touch switch range selection. Model 7045 measures pH to 0.01, has a relative mV scale with 0.1 mV resolution for ion selective electrode measurements and offers an absolute mV range (0-1440 mV) for titration procedures. Temperature readout is available in conjunction with a Pt 100 resistance thermometer and both automatic and manual temperature compensation operate over the full 0-14 pH range.

Reader Enquiry Service No. 43

#### **Flame retardant**

A new range of zinc borates, manufactured by the Humphrey Chemical Corp., are to be distributed exclusively under the Garoflam trade mark by Croxton and Garry Limited in the UK.

The range consists of five grades which act as flame retardants and after-glow suppressants in plastics, rubber and paints. When heated, zinc borate loses its water of crystallisation as steam; further heating in the presence of chlorinated organics causes hydrolysis of the zinc borate to zinc chloride and boric acid which fuse over the substrate surface. Both these actions retard flame propagation and the final salts act as after-flow suppressants, preventing re-ignition of the charred material surface. Reader Enquiry Service No. 44

#### New inks for small offset machines

An important breakthrough for all small offset machine users is claimed by Fishburn with the introduction of Fishburn Rialto (SO) Pantone inks. The company states that this is the opinion of printers who have made exhaustive trials.

The print performance of this new generation of small offset rubber-based inks is described as outstanding, resulting from the latest compatibility research into resin, varnish and pigment technology. Reader Enquiry Service No. 45



## Nail lacquer filling machine

The latest machine to be developed by the Universal Filling Machine Co. is specifically designed for nail lacquers.

By its very nature, this semi-liquid product has presented difficulties to cosmetics manufacturers but with the 2-Head Easifill machine its large bore feed pipes and specially constructed nozzles it is possible to achieve filling speeds in excess of 2,000 bottles per hour.

The unrestricted flow system of the Easiclean nozzles and the careful balancing of tube sizes allows high speed filling whilst totally eliminating dripping when the bottles are removed.

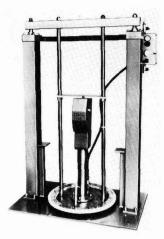
Plastic tubing is specially selected for its resistance to the acetone base of the product and the special wide mouth interceptor jar system of overflow return allows the system to be quickly cleaned when the filling session has been finished.

Flameproofed motors and switchgear are fitted as standard and the machines retain the standard flexible head system to reduce operator fatigue. Reader Enquiry Service No. 47



Filling machine for nail lacquers





The Kencol Maxiprime

#### New dual post ram

Kingdom Engineering Co. Ltd have developed a large capacity dual post ram for the efficient emptying of standard 45 gallon (200 kg) open top drums.

The Kecol ram, known as the Maxiprime, will eliminate waste and spillage, even on the most highly viscous and difficult of products. The follower plate is designed for efficient cleaning of the drum sides and to leave a minimum amount of waste in the bottom of the drum.

The Maxiprime is built for long life, even with robust usage, and has a cushioned stroke giving extremely quiet operation.

Reader Enquiry Service No. 48

### New resin from Synres

Synres has developed a new resin. It is described as a methylated melamine formaldehyde resin, non-plasticized. It is a high solids type with excellent compatibility, fast cure response, low formaldehyde emission and good gloss.

It is intended for general purpose low bake stoving enamels, domestic appliances, high solids stoving enamels and water reducible stoving enamels. *Reader Enquiry Service No.* 49

#### New Atlantic range of dyes

Atlantic Chemical Corp. has announced the addition of a new series of dyes called the Atlamet range.

The Atlament dyes are a 2:1 premetallized molecule with, it is claimed, excellent cold water solubility and good fastness properties.

The Atlamet range is recommended by the manufacturer for the dyeing and printing of nylon and wool, where premium quality and fastness requirements are essential. This highly-soluble range of colours can be dyed from a neutral system offering the dyer excellent levelness and penetration.

Atlantic also reports that the new range show excellent uniform dyeing characteristics with blends of nylon and wool.

The Atlamet range is recommended for use on carpets, curtains, upholstery, automotive fabrics, uniforms and clothing. The range is also recommended for top-grain and split leather, where high light fastness and wet fastness is required. *Reader Enguiry Service No. 50* 

#### Average-quantity packaging

A new statistically-based sampling packaging control system called Compupak has been announced by International Electronics Ltd. It is intended for packers operating on the average quantity system.

Compupak is a purpose-built weighsampling system combining great power and versatility with simplicity of operation and low investment cost.

The built-in statistical routines and printed record formats have been designed by an expert in both process control and the average quantity system. The routines comply not only with legislative requirements that require no underfill, but also reduce overfill to a minimum. All the necessary calculations are worked automatically, including the derivation of precise process adjustment instructions from package samples, allowing a rapid response to the need for adjustment and enabling process operators and quality control staff to concentrate on controlling the packing line itself and not interpreting the control system results. Reader Enquiry Service No. 51

### New thermometric titration unit

One of the first products to be introduced following the recent formation of Ultra Scientific and Design Ltd from the amalgamation of two companies, is a thermometric titration unit.

The instrument is based on equipment designed by Professor L. S. Bark of Salford University and is equally suitable for routine analysis, teaching and research purposes. It can be used for both thermometric and enthalpimetric analysis.

Included in the features of the instrument is a built-in peristaltic pump which delivers titrant at a rate of 6 ml per minute with good reproducibility. The transistorised circuitry of the instrument is based on a modular design concept allowing for presentation of results on the built-in digital meter and/or on a standard single pen chart recorder. Reliable temperature measurement is assured by the presence of a high grade thermistor probe with virtually instantaneous response time. The instrument is thermally insulated by mounting the titration vessel in an insulated matrix, thus effectively eliminating errors due to thermal leakage. A built-in variable speed magnetic stirrer is included which obviates risk to the glass thermistor temperature probe.

Reader Enquiry Service No. 52

#### Increased filter efficiency from a "continuous wicking gel"

Air filtration systems will only function efficiently if they are regularly serviced, cleaned and lubricated. A highly effective filter adhesive for use in this process is Droyt HD 52K from the Lubricants Division of the Witco Chemical Co. It is a specially developed coating designed to assist in the actual filtration process whilst also protecting the metal panel filter against corrosion.

The adhesive acts as a "continuous wicking gel" structure. This has the effect of wetting down the dirt particles caught in the filter and this new wet surface provides additional area for catching dirt particles. Best results are obtained by immersing the filters in a bath of HD 52K after thorough cleaning and draining. Laboratory and on-site tests show that this adhesive immersion is the most effective way of getting a uniform coating through the filter.

It can also be applied by brush or spray, and will give protection against toxic gases, corrosion and oxidation for periods of up to 18 months. It will not drip at temperatures in excess of 200° and is efficient at sub-zero temperatures. It is a highly tenacious, non-melting, chemically inert film. When necessary it can be removed by immersing the panels in a hydrocarbon solvent. *Reader Enguiry Service No. 53* 

#### New range of agitators

Gee and Co. (Effluent Control) Ltd, specialists in the design and construction of effluent treatment systems, is launching a range of mechanical agitators.

These units are available ex-stock, in variations to suit most process requirements. Robustly constructed, yet

economical in cost, the standard range is suitable for tank capacities up to approximately 2,500 gallons, with units for larger capacities manufactured to suit customer requirements.

Standard specification includes stainless steel ground bar shaft checked for balance and run out, and an individually machined flange type coupling to ensure maximum strength, rigidity and performance. All immersed parts are PVC coated for chemical resistance. Motor units, size and pitch of propellers are matched to process fluid and duty.

Units are available for duties as diverse as chemical reactions where turbulence is required or blending dissolving and suspending operations which demand high bulk turnover, as well as for general purpose applications. *Reader Enquiry Service No. 54* 

### New paint application idea

Berger Paints and Black & Decker have introduced a new concept in home decorating called Paintmate. It comprises a new range of paints and a new method of applying them.

Paintmate works by feeding paint directly from a tub to a roller, brush or paint pad. A push button activates a simple soda syphon bulb to feed the paint to the painting head at the required rate, as and when the painter needs it. *Reader Enquiry Service No. 55* 



Push button painting with Paintmate



The Paintmate system showing roller, brush heads and paint pads literature

## Selection of biocides for emulsion paint

Thor Chemicals Ltd have published colour illustrations of the test procedures used to assist both home and overseas emulsion paint customers, in the correct selection of type and quantity of biocides. *Reader Enquiry Service No. 56* 

## Ignitability of building products

The British Standards Institution has published DD 70 "Method of test for ignitability of building products", which is a new draft for development which describes one of a series of tests being developed, in co-operation with the International Organisation for Standardisation, to assess the contribution made by various building materials towards the growth of fires.

DD 70 provides a method of test for examining the ignition characteristics of the exposed surfaces of essentially flat materials, composites or assemblies when fixed on a horizontal plane and subjected to specified levels of thermal irradiance. The test differs from that specified in BS 476 Part 5, in that it can be used to measure the ease of ignition of a product when subjected to defined levels of thermal irradiance, thus representing increasing levels of fire growth. *Reader Enquiry Service No.* 57



## **Call for papers, corrosion testing**

"Electrochemical methods in corrosion testing and research" is the title of an International Conference to be held at UMIST, 4-6 January 1982. The meeting is intended to cover recent advances in the use of electrochemical techniques in corrosion and allied fields.

Further information is available from: Dr F. A. Cottis, Corrosion and Protection Centre, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England.

### 19th New Zealand convention

The Auckland Section of OCCA is to hold the highly successful New Zealand Convention, it will be held at the Rotarua International Hotel on Thursday 30 July – Sunday 2 August 1981. This year's Convention, the 19th, has as its theme: "Over-view concerning cladding alternatives" (the acronym of which is "OCCA"). Further information is available from OCCA Auckland, Convention Organising Committee, PO Box 5192, Auckland, New Zealand.



## Vehicle refinishing seminar

The Thames Valley Section will be holding a one day seminar entitled "Vehicle refinishing" on Thursday 22 October 1981, to be held at the Lorch Foundation near High Wycombe. Full details will be announced later.

## Northern Sections' golf tournament

The northern sections of OCCA will be holding a golf tournament on Thursday 25 June 1981. Further details are available on page vi.

#### London Section's golf tournament

The London Section of OCCA will be holding a golf tournament on Wednesday 8 July 1981. Further details and an application form are available on page xiii.



Miss Ann Mansell has relinquished her position as managing director of Arthur Sanderson and Sons Ltd. Mr Malcolm Glenn, managing director of Reed Decorative Products and chairman of

Arthur Sanderson and Sons Ltd, will act as managing director until a permanent replacement is announced.

Mr David C. Walsh, group managing director of Ellis & Everard Ltd, will take over as divisional managing director of the group's Fine Chemicals Division at the end of August on the retirement of Mr Douglas F Anstead, the present divisional managing director.

Warwick Chemical Ltd has appointed **David Smith** to the newly-created post of chemical product manager, based at the company's Mostyn plant in North Wales.

Cabot Carbon Ltd have announced the appointment of John F. McKeown to the position of sales representative for the North of England and Scotland.

Mr McKeown's previous experience is in the paints, paper and pigmentation fields and he is assuming the sales responsibilities previously carried out by Peter Gallagher. **Mr Gallagher** has now taken up his new appointment of technical service work on special blacks in the UK and certain European markets.



## **Reader Enquiry Service** expanded

For sometime now JOCCA has had a *Reader Enquiry Service*, enabling readers to obtain further information on articles that have appeared in the Journal, by simply circling the appropriate numbers on the form that appears at the back of the Journal and sending it, or a photocopy, to the Association's offices.

Due to the great interest shown so far, it has been decided to expand the scope of this service. As from now advertisements will be included in the scheme and there will be no limit on the number of enquiries per form.

# Manchester Section

## Informal buffet dance

The informal buffet dance was held this year, as in previous years, at the Royal Air Force Association Club, Sale, Cheshire. One hundred and forty-seven members and their guests attended this year's event on Friday 6 March 1981. Dancing commenced at 8.00 p.m. to the generous decibel rating of The Axis group and disco. An excellent buffet was served at 10.00 p.m. followed by further dancing until the established practice of coin rolling towards the centrally located target of a full whisky bottle, which raised £26 for the RAF Wings Appeal.

The winner, Jim Ashworth of Crown Paints, generously donated his prize for auction and a further  $\pounds 10$  was raised for the RAF charity.

Dancing recommenced and continued to 12.30 a.m., at which time the 1981

For information on membership of OCCA, enquiries should be sent to the Association's offices, see front cover for address.

informal buffet dance was satisfactorily concluded, organised by section members David Clayton and Arthur Thornhill.

F.B.W.

## **Midlands Section**

## Work of the National Trust

The annual ladies' invitation lecture of the Midland Section was held on 19 March 1981 at the Birmingham Chamber of Commerce and Industry, Harborne Road, Birmingham.

After a very enjoyable hot buffetsupper, members, their ladies, and guests heard Mr A. C. P. Ford, assisted by his wife, give a talk entitled "Work of the National Trust".

Mr Ford opened his talk by saying that the National Trust is a charity which depends for its existence on the enthusiasm and generosity of its donors, voluntary members and the general public. The Trust was founded in 1895 as a public company to acquire and preserve for the Nation, places of historic interest or natural beauty. In 1937 an Act of Parliament enabled the Trust to hold the great country houses and their contents as well as land and ancient buildings. The country house scheme, as it became known, enables a country house to be donated to the Trust, together with an adequate endowment fund to maintain it in perpetuity. In return, the donor and his descendants may go on living in the house rent free, subject to public access and to certain controls to ensure that the original character of the property is preserved.

Mr Ford then handed over to his wife who, with the aid of a large collection of coloured slides, took the audience on a grand tour of many of the Trust's properties. These properties include gardens, windmills, theatres, country houses and whole villages. The Trust also owns large areas of land in the Lake District, Snowdonia and the Brecon Beacons. In 1965 the Trust launched a scheme called "Enterprise Neptune" to acquire those parts of the UK's coastline that were beautiful and unspoil by development. To date the Trust has acquired some 400 coastal miles. In conclusion, Mr Ford said that the National Trust was divided into over 100 Trust Centres. These centres were local groups of Trust members who supported the Trust and arranged lectures, films and visits for their membership.

The meeting closed with a vote of thanks proposed by Mrs V. Devenish which was applauded by the audience.

B.E.M.

## Obituary

Jack Smethurst

Mr R. S. Monk writes:

I first knew Jack when I left school to work as a laboratory assistant in 1954. Jack was then the driving force of a rapidly growing company in an expanding market.

He gave total effort to any task in hand and demanded the same total effort, enthusiasm and dedication from all his staff, accepting no excuse for anything less than the best.

The years passed and Jack's stature in the industry continued to grow and I then had the experience of feeling the impact of J.S. as a competitor -a hard, uncompromising adversary but always straight and fair - not predictable, but a man of integrity.

Over the past few years, Jack became a colleague who, despite ill health, gave the same dedicated effort which had been evident throughout a highly successful career and provided a model for all to follow.

Most important of all, I knew Jack as a friend, a friend who could be relied on to offer the same dedicated effort to help solve problems, not only in business, but problems of a personal nature.

Not only has industry lost a most dynamic and dedicated character, but we who have had the privilege of knowing Jack have lost a true friend.

I offer my sincere condolence on behalf of all my colleagues to Mrs Smethurst and family.

## **Report of the Council Meeting**

A meeting of the Council of the Association was held on 8 April 1981 at the Great Northern Hotel, Kings Cross, London NI at 2.00 p.m. with the President, Dr F. M. Smith in the Chair. There were 25 members present. Mr D. S. Newton was nominated to serve on BSI Committee PVC/1/10 Miscellaneous Pigments, in addition to Mr W. B. Cork. It was reported that Mr P. Gallagher represented the Association on BSI Committee PVC/1/9 – Black Pigments. It was reported that Dr L. Simpson would present a paper to be designated as this Association's paper at the FSCT Convention (Detroit, 28-30 October 1981), that T. R. Bullett (or another member from the Paint Research Association would present a paper at the SLF Convention in Copenhagen 11-13 October 1982 and that Mr J. Clark would arrange for a paper to be given at the FATIPEC Congress at Liege 9-14 May 1982.

The President briefly described the details of the OCCA International document which had arisen from a Working Group at the end of 1980 and it was agreed to accept this as a reference document for future discussion.

Preliminary arrangements for the 1982 AGM were discussed and it was agreed to follow the format of the 1978 and 1980 Luncheon Lectures, coupled with the Council Reunion, prior to the AGM on a date in June 1982.

The Annual Accounts for 1980 and estimates for 1981 were tabled, discussed and adopted, and membership subscription rates were agreed. It was further agreed that the names of members whose 1981 subscriptions had not been received by 30 June should be removed from the Register. Council was pleased that the percentage of those in arrears with subscriptions, during a difficult period, was no higher than at a comparable date in April 1980.

Reports were received on the arrange-

ments for the 1981 Exhibition (OCCA-33) and the Bath Conference (17-20 June 1981). Both these Association events were discussed fully, it being noted that a number of other exhibitions had been cancelled, curtailed or postponed: that the Official Guide and the April (Preview) issue of the Journal had already been received or would shortly be received by members and that considerable interest had been shown by non-members in the Conference. The Council congratulated the Director & Secretary on the marketing of OCCA-33 and it was reported that constant enquiries were being received from potential visitors.

It was reported that the 1979-80 Jordan Award would be conferred upon Mr M. W. Leonard for his paper which had appeared in the December 1979 issue of the *Journal*, this paper being based upon the dissertation successfully submitted by Mr Leonard for Licentiateship in the Professional Grade.

The President and the Honorary Technical Education Officer reported on the present stage of discussions with trade associations on educational matters and it was reported that the Honorary Technical Education Officer intended to set up two small working groups to study specific problems.



The Director & Secretary reported that six Ordinary Members had been admitted to the Professional Grade – five as Associates and one as Licentiate.

Under Section Reports, the Hull Section Chairman (Mr P. W. Munn) stated that it was intended to hold a joint meeting with the West Riding Section at least once in each session.

Votes of thanks were recorded to the Retiring President, Retiring Honorary Research and Development Officer and others retiring from Council.

There being no other business, the President thanked members for their attendance and declared the meeting closed at 4.27 p.m.

## The President's Page

As I near the end of my term of office, it seems an appropriate time to comment on important issues again.

## South Africa

In my last commentary, I referred to the excellent reception which Dorothy and I received at the OCCAA Convention in Adelaide and the OCCA New Zealand Convention in Rotorua in mid-1980. Since then, we have attended the South African Annual Symposium in Durban, Natal. This was an equally wonderful gathering enhanced by the fact that there are few opportunities between annual events such as these for other get-togethers. Truly memorable hospitality.



I was able to present the keynote address at the Symposium on "The outlook for the eighties", which has been published in the April issue of JOCCA. It has aroused considerable interest, both at the time and subsequently, and is, I

1981(6)

believe, a useful background paper for considerations of the future of OCCA. At meetings in Johannesburg and Salisbury I



was also able to give lectures to local sections, and meet many of our members. In Zimbabwe in particular, I was able to see the keen interest and to appreciate the help we are able to give, through Robert Hamblin and our HQ staff, to small and sometimes isolated groups.

## Subscriptions

In the 1960s and 1970s, our subscriptions were never sufficient to maintain our organisation, which is of course exclusively for individual professional membership. However, we were always able to make useful contributions from our Journal, from advertising, from symposia run by the UK sections, and from the Exhibition. Modest increases in subscriptions were always judged carefully to be what the market would bear without losing members. Now we are rapidly coming to a situation where membership numbers are declining slightly, symposia are less well attended, and the Exhibition is diminishing in importance. We have already taken significant economy measures by stopping the sending of circulars for UK section meetings; this could put greater demands on section officers to keep their affairs alive and active.

Opinions vary on the future of the Exhibition, but if it cannot produce a positive contribution on average, then we are heading for a difficult financial situation. Raising subscriptions to bridge the gap is hardly likely to be popular, and would unquestionably reduce membership. Higher postage costs are also having a very adverse effect on the costs of distributing the Journal, both at home and overseas; overseas postage at 48p per issue makes a big bite into any subscription. And the Journal is obligatory for every member.

As a consequence of this situation, we shall have to do some very radical forward thinking. Times are changing and we must move with them.

#### Education

One serious impact of a depression is the reduced demand for technically trained personnel and the, partly consequential, reduction in the number of teaching establishments. Our view is that only a



few centres will remain in the UK, and then only if the industries concerned, and OCCA as a qualifying body, take some initiatives. I am happy to say that this is exactly what we are doing and the response from trade associations is so far very encouraging. Follow-up action will be required rapidly before it is too late.

We have in mind a Graduateship and a Technicians' (Higher) Diploma, and would eagerly go into the publication of training literature.

## Conference

The OCCA Conference is a unique event which meets a limited need. It would be a pity to see it disappear and, so far, there is no immediate danger of this. Any decision to hold a conference or symposium in conjunction with an exhibition might, of course, have an impact on it. This idea could be one way of helping to revitalise the Exhibition and would not adversely affect section symposia, which are already badly hit. Our move to centres of historic interest – Stratford and Bath – appears to be more attractive than the declining seaside resorts.

This year's discourse, on alternatives to paint, should prove very stimulating and provocative to paint makers looking for new ideas. We are indebted to Manchester Section for their first successful venture into a discourse.

## **OCCA** international

Council has agreed to this concept in principle, as a means of bringing together all members, whether of OCCA or OCCAA, and to encourage the link by means of an international conference every six years. The first was to be held in Singapore in 1983, but it is judged by our friends in Australia to be unlikely to command sufficient support from the Far East. It is essential that there is an international forum to work out points of detail, especially on such knotty problems as the equivalence of professional qualifications. Although each country has its own peculiar problems, there is no doubt that the old adage still applies - united we stand, divided we fall.

## Administration

Many associations thrive and perhaps only continue to exist due to the devoted service of one man. In our case this is so with Robert Hamblin, who for 30 years has carried us along and been the lynch pin of the international connections and the helping hand to the individual member, wherever he is. Presidents come and go and, so far, Robert Hamblin has gone on and on. We are planning the introduction of an assistant secretary to help preserve our mainstay.

## Conclusion

I am writing this in anticipation of a successful Conference in Bath, and continuing enthusiastic support for Don Morris, who is to be made our new President at the AGM. Thank you all for your support during my two years and your welcomes wherever Dorothy and I have been.

And finally, may I say that OCCA will only continue to prosper if we make brave moves into the future which will justify an active extension of our membership.

F. M. Smith



## **Ordinary Members**

- ANDERSON, PETER HAROLD HARTMAN, 8 Timber Street, Wentworth Park, Krugersdorp, South Africa (Transvaal)
- BENTLEY, PHILIP ANTHONY, BSc, Blundell Permoglaze Ltd, Sculcoates Lane, Hull (Hull)
- BRADLEY, SCOTT WARNER, BSc, PO Box 1084, Auckland, New Zealand (Auckland)
- CHANA, HARCHETAN, 18 Simsbury Court, Markham, Ontario L3R G37, Canada (Ontario)
- CUMBERS, ALAN MICHAEL, Carless Solvents, Hepscott Road, London E9 5HD (London)
- EDWARDS, C. J., BSc, 8 Yeoman's Close, Milnrow, Rochdale, Lancashire OL16 3UP (Manchester)
- ELLIS, HUBERT GEOFFREY, BSc, PO Box 91, Gallo Manor 2052, South Africa (Transvaal)
- FUERY, MICHAEL JAMES, Athlone Manufacturing Ltd, Cornamaddy Industrial Estate, Athlone, Ireland (Irish)
- HARRISON, STEPHEN, BSc, Blundell Permoglaze Ltd. Sculcoates Lane, Hull (Hull)

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

- HOLMES, VICTOR NOEL, BSc, c/o Sidney Cooke Chemicals, PO Box 58-005, East Tamaki, New Zealand (Auckland)
- LINDSAY, DOUGLAS MICHAEL, 3, 12th Street, Parkmore 2196, South Africa (Transvaal)
- LOFTHOUSE, ROY, PhD, CChem, MRSC, BOC Chemicals, Vigo Lane, Chester-le-Street, Co Durham (Newcastle)
- PLUMMER, DAVID JOHN, Holden Surface Coatings Ltd, Bordesley Green Road, Birmingham B9 4BQ (Midlands)
- SCHAFLI, PATRICK WILLIAM, BSc, AECI Paints (Pty) Ltd, 166 Bluff Road, Jacobs, Durban 4052, South Africa (Natal)
- VERMA, RATNAKA PRASAD, BSc, MSc, N-92/1 Telco Colony, Jamshedpur-831004, India (General Overseas)
- WADDINGHAM, DONALD MARKHAM, BSc, MNZIC, Tergo Industries, PO Box 47111, Auckland, New Zealand (Auckland)

#### Associate Members

- BALDOCK, MALCOLM, England Hughes Bell & Co Ltd, Monton Road, Eccles, Manchester M30 9HJ (Manchester)
- GRAY, MICHAEL, 43 Lyndhurst Avenue, Hazel Grove, Stockport, Cheshire SK7 5LT (Manchester)
- SEARLE, EDWARD JACKSON, PO Box 50669, Randburg 2125, South Africa (Transvaal)

## CLASSIFIED ADVERTISEMENTS

## **APPOINTMENTS**

# Physical Chemist

Taylor Woodrow Research Laboratories, located at Ruislip Road, Southall, require a Chemist to join a small but expanding Chemistry Group undertaking a range of interesting testing and analytical work. Activities are related to technical problems within the Company in addition to research contracts for offshore, liquid gas storage and nuclear developments.

Applicants should be about 30 years of age, possess a chemistry degree, and have an interest in chemical/physical processes and the mathematics involved, together with experience in standard instrumental techniques (e.g. gas chromatography, flame photometry, x-ray diffraction etc.).

A competitive salary will be accompanied by first class conditions of employment. For an application form, please contact:

Peter Stoner (Ref. RDB), Taylor Woodrow Construction Limited, 345 Ruislip Road, Southall, Middlesex UB1 2QX. Tel. 01-575 4286.



## SITUATIONS WANTED

## SENIOR POSITION REQUIRED

Hons. degree paint chemistry, LRIC, Professional Grade OCCA, 16 years experience surface coatings and pigment dispersions; senior R & D, quality control, technical service, works liaison, technical management. N. England preferred.

Please reply to Box No. 499

## QUALIFIED & EXPERIENCED PAINT CHEMIST

Qualified paint chemist (graduate, 29) with substantial experience in quality control, formulations, production, laboratory set-up, product development, colour match, technical service, etc. seeks a challenging position (UK), most locations considered, SE England preferred. NB also experience of plastics, electroplating and teaching, *Please reply to* **Box No. 500** 

## Building Materials Technologist

## **Research Laboratories**

Taylor Woodrow Research Laboratories, located within travelling distance of rural Buckinghamshire, are undertaking an ever increasing and diversifying work-load.

In order to meet our targets, we require a suitably qualified person to establish the performance and use of building materials and products both in the laboratory and under field conditions.

Applicants will probably hold a physics or chemistry qualification, and possess the ability to investigate situations, specify and supervise tests and analyse results, and prepare technical reports to meet clients requirements.

This is not a routine laboratory position, and the holder will have to possess the ability to apply original thought in order to achieve practical solutions within sound scientific and commercial guide-lines. Every encouragement will be given for the successful candidate to develop his/her team in order to increase his/her own and the laboratory's horizons.

Although based at Head Office, travel throughout the United Kingdom with short periods overseas will be required.

An attractive salary will be negotiated and accompanied by the conditions of service to be expected with a large international organisation.

For more information and an Application Form please contact: Peter Stoner (Ref. RDB), Taylor Woodrow Construction Limited, 345 Ruislip Road, Southall, Middlesex UB1 20X. Tel: 01-575 4286.



## **APPOINTMENTS**

## **Paint Technologist**

Required for paint company in South Africa, must be fully experienced. Interviews in London in the middle of July. *Please write with full details* to **Box No. 502** 

## **RECONDITIONED EQUIPMENT FOR SALE**

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

Flame-protected to Group 2 (gases and vapours). Counterbalance and Pedestrian types available. Suitable for Chemicals, Paints and allied industries. Re-conditioned to an exceptionally high standard. Issued with load test certificates and guaranteed.



## Speed Electrics, Wells Road, Nottingham Tel: 0602 609782

## LICENCE AVAILABLE

## AVAILABLE FOR LICENCE

US manufacturer offers licence for the formulation of catalyzed, twocomponent, traffic safety paints having 99 per cent solids content by volume.

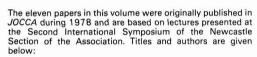
Please contact: President, DeSantis Coatings Inc., 4580 Beidler Road, Box 160, Willoughby, OH, 44094, USA.

## OIL & COLOUR CHEMISTS' ASSOCIATION



## ULTRAVIOLET POLYMERISATION AND THE SURFACE COATING INDUSTRIES

Newcastle Section Symposium



- 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 photoactivators by M. J. Davis, J. Doherty, A. A. Godfrey, P. N. Green, J. R. A. Young and M. A. Parrish

Copies of **UV Polymerisation**, the first volume published by the Association on this subject, are available and may be purchased separately or at the specially reduced price if purchased together with a copy of *UV2*.

The two volumes together form the authorative work on the rapidly developing subject of ultraviolet polymerisation in the surface coatings industries. It is a work that no company in the field can afford to be without.

## ORDER FORM

To: **Oil & Colour Chemists' Association**, Priory House, 967 Harrow Road, Wembley, Middlesex HAO 2SF, Engla.1d.

Please send me .... copies of Ultraviolet polymerisation 2 (UV2)

Please send me .... copies of Ultraviolet polymerisation (UV1)

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

Name: \_\_\_\_

Address to which books should be sent:

Price: Ultraviolet polymerisation 2 (UV2) £7.50 (US \$18.00) each

Ultraviolet polymerisation 1 (UV1)  $\pm 5.00$  (US \$12.00) each

UV1 and UV2 purchased together £10.00 (US \$24.00)

Prices include postage/packing (surface mail)

## OIL & COLOUR CHEMISTS' ASSOCIATION LONDON SECTION

## **1981 LONDON SECTION GOLF TOURNAMENT**

Course: Canons Brook Golf Club, Harlow, Essex. Tel: Harlow (STD 0279) 21482.

Date: Wednesday 8 July 1981.

Starting time: Tee reserved from 1.45 p.m. onwards - 3 player grouping at 6 minute intervals.

- Type: Singles Stableford. Handicap allowance 7/8. Maximum allowance 18 strokes. Competitors will play off their lowest club handicap. Any competitor not having a current club handicap will be allocated one, prior to starting, by a Sub-Committee.
- **Cost:** £15.50 per head (cheque made out to OCCA-London Section) covering the cost of green fees, buffet lunch, evening meal, sweep, gratuities and VAT.
- **Catering:** A buffet lunch will be available between 12 noon and 2.00 p.m. An evening dinner has been arranged at which presentation of the prizes will also take place.
- **Eligibility:** All OCCA members and their guests. Maximum number of entrants will be 60. Preference will be given to OCCA members. Notification of withdrawal from the competition to be made to the undersigned as soon as possible.
- Prizes: Offers of prizes to add incentive to the competition will be greatly appreciated.

Application: Members wishing to take part are requested to return the attached slip plus £15.50 remittance as soon as possible, and no later than 30 June 1981.

**1981 London Golf Tournament** 

To: Mr A. J. Newbould, Hon. Secretary, London Section, 30 Windsor Road, Worcester Park, Surrey KT4 8EW Tel: 01-476 3031 (business) 01-337 3553 (home) I/we wish to enter the London Section Golf Tournament I/we will require ..... buffet lunch(es) I/we will require ..... evening meal(s)

NAME

MEMBER OR NON-MEMBER

HANDICAP

I enclose a remittance for £ .....

NAME	
ADDRESS	BLOCK LETTERS PLEASE

.

Cheques must be made payable to "OCCA-London Section"

JOCCA				
READER ENQUIRY S	ERVICE – JUNE 1981			
For further information circle items listed below:	Name			
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60	Job Title			
61         62         63         64         65         66         67         68         69         70         71         72         73         74         75         76         77         78         79         80           81         82         84         85         86         87         88         90         91         92         39         94         95         96         97         80         99         101         102         103         104         105         106         107         108         109         110         11         112         113         114         15         16         17         118         19         120           101         102         103         104         105         106         107         108         109         110         11         112         113         114         15         16         17         118         19         102           102         102         124         124         126         127         123         134         15         163         15         15         15         15         15         15         15         15         135         15 <td>Company</td>	Company			
12 1 12 1 13 124 125 126 127 128 129 130 13 1 127 133 134 135 136 137 138 139 139 1 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200	Address			
Please also send information on the following items relating to the above:				
	Country Telephone			

## Journal of the Oil and Colour Chemists' Association

Priory House, 967 Harrow Road, Wembley, Middx., HA0 2SF, England Telephone: 01-908 1086 Telex: 922670 (OCCA G)

## AT ANY TIME DAY OR NIGHT TELEX YOUR CLASSIFIED FOR JOCCA

Telex 922670 (OCCAG)

## **INDEX TO ADVERTISERS**

Further information on any of the products advertised in this *Journal* may be obtained by circling the appropriate number on the *Reader Enquiry Service (RES)* form above. The *RES* numbers are shown in brackets below. Enquiries will be forwarded to the organisations concerned.

\_

-

E ECC International Ltd (101)	i	N NL Chemicals	iii
G George Reffold (102)	Cover	<b>O</b> OBS Machines Ltd (108)	Cover
H Hillwood Ltd (103)	Cover	<b>P</b> Paint Research Association(109) (110)	Cover Cover
ICI Mond Division Ltd (104)	viii & ix	0	
J Johns-Manville(105)	vii	Q-Panel Ltd(111)	Cover
		S	
<b>K</b> Kemira Oy(106)	x	Sanyo-Kokusaku Pulp Co. Ltd (112) Servo BV	iv Cover



# Guide to Preservatives for Water-Borne Paints

Following the favourable response to the earlier Paint RA special publication, GUIDE TO PAINT FILM FUNGICIDES, published in July 1979, it became apparent that there was a need for a companion guide to the preservation of water borne paints and paint components against microbial spoilage.

For this special publication, over five hundred potential suppliers of preservatives world wide were contacted. As a result, comprehensive data, both chemical and toxicological, has been collected and tabulated on 130 commercially available products. The guide also includes a critical review of current literature on water borne paint spoilage and preservation.

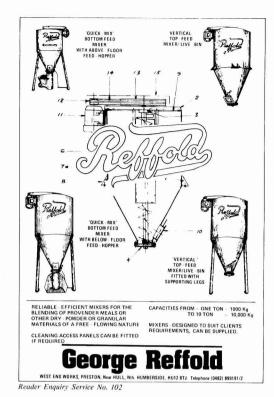
It has not been possible to list preservative activity, even in comparative terms as this, to a great extent, is dependent upon the product in which the preservative is to be used. The aim of the guide is primarily to enable the user to select a short-list of potentially suitable products prior to further testing for compatibility and preservative activity.

It is hoped that this guide will be of use not only to the paint industry and its suppliers and customers, but also to many other industries handling water based products.

Price: £25 (Paint R.A. Members - £10)

Available from Mrs Caroline Veitch Publications Co-ordinator Information Department Paint Research Association Waldegrave Road Teddington, Middlesex TW11 BLD

Reader Enquiry Service No. 110



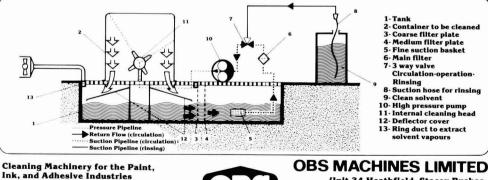
Clean up with KAREHER & OBS

Cleaning problems are a thing of the past when you install K'a'rcher high pressure, solvent alded cleaning equipment. The most problematic deposits on Mobile Vessels, Fixed Vessels, I.B.C.'s, Tote Bins and Pots can be quickly removed, and complete inplant cleaning systems can be supplied. Cost savings are achieved by efficient cleaning processes, and K'a'rcher expertise also ensures that manufacturers keep abreast of Health and Safety regulations, particularly where caustic chemicals and other dangerous substances are utilised. Contact OBS now for full details of the

superbly engineered range of cleaning systems from K'a'rcher.







D.7057 Winnenden/Württ, West Germany

Alfred Kärcher GmbH & Co.,

Unit 34 Heathfield, Stacey Bushes, Milton Keynes MK12 6HR Tel: Milton Keynes (0908) 313186 or 313373 Telex: 825663 (088UK G)

Reader Enquiry Service No. 108

## **Pigment dispersant** SER-AD FA 6

SER-AD FA 601 accelerates and improves wetting and dispersion of pigments in organic solvent containing systems. SER-AD FA 601 improves the tinting strength, for instance of (expensive) organic pigments, which results in a lower cost price of the paint.

## EXAMPLE

1.0 0.7 0 A В without dispersant with dispersant

## 

We export paint additives to over 93 countries.

A-required amount ofchinacridonviolet

ofchinacridonviolet for the same colour

in a paint with SER-AD FA 601:

in a pastel paint without dispersant: 1.0% **B**-required amount

0.7%

## France Ets G. Thévenot

14, Rue de Moscou 75008 PARIS Telex: 641666

Switserland Acima AG für Chemische Industrie CH-9470 BUCHS Telex: 74284

Austria Acima Chemische Produkte GmbH Postfach 23 A-1182 VIENNA Telex: (0) 136155

Portugal Ahlers Lindley Lda. R. Do Ferragial 33 <sup>20</sup> P.O. Box 2884 LISSABON 2 Telex: 12570

United Kingdom + Ireland M.L. Chemicals Ltd. Bridgeway House Mellor Road CHEADLE HULME Cheshire SK 85 AU Telex: 666475

Carribean-Central America Chemo Supply P.O. Box 151 ISLINGTON, Ontario Canada M9A 4X2 Telex: 06-967645

rvo bv-delden



Reader Enquiry Service No. 113

