JOURNAL
OF THE
OIL AND COLOUR CHEMISTS' ASSOCIATION

Vol. 52 No. 5 **May 1969**

Effect of inhibiting pigment in high-build chlorinated rubber systems for underwater use
T. F. Birkenhead

The formulation of zinc oxide latex paints
E. Hoffmann and A. Saracz

Electron probe analysis in the investigation of surface coating problems
P. Whiteley, K. E. Fletcher and G. W. Rothwell

The influence of the solvent and of the substrate on the water vapour permeability of films
R. Katz and B. F. Munk

21-OCCA REVIEW

OIL & COLOUR CHEMISTS' ASSOCIATION
WAX CHANDLERS' HALL,
GRESHAM STREET, LONDON, E.C.2

Dynamit Nobel chemicals serve the coating industry

DYNAPOL
Saturated terephthalic acid based polyesters suitable for punched and deep-drawn, sterilizable, boil-proof, weather-resistant lacquers and printing inks.

ICDAL®
Alkyd resins for the formulation of high quality industrial and decorative lacquers, stoving and nitrocellulose blended lacquers.

HYDRO-ICDAL®
Water soluble alkyd or epoxy resin esters suitable for both conventional stoving lacquers and for use in electro-phoretic application.

ICDAL® TE/TI
Electro-insulating enamel resins, terephthalate as well as ester imide based, for the preparation of temperature resistant insulated conductors of types N and W (DIN 46 453 wire lacquer resins) and insulating lacquers (VDE-norm 0360 or DIN 46 456 dipping lacquers).

Hydrolizate H 400 and H 450
Binders for zincdust paints.

Alcohol Wet Nitrocellulose Plasticised Nitrocellulose
(Cellulose Nitrate, Technical grade)

Finishes for wood:
Lacquers for furniture, floor, cardboard, pencils and household goods.
Finishes for metal:
Zapon, machinery camouflage, automotive and aircraft lacquers, for toys, industrial products and household goods.
Coatings for flexible substrates:
Paper, cardboard, fabric, leather, film of regenerated cellulose and aluminium foil.
Numerous other uses as in printing inks, adhesives and nail polish.
Application of the lacquers by spray, hot spray, brush, blade, dip, roller, aerosol, emulsion-coating.

Titanium as well as Vanadium and Zirconium Esters
Binders for corrosion-proof high-temperature resisting lacquers and varnishes (400° to 600° C).

Reactive cross-linking agents and hardeners for lacquer resins like alkyd, epoxy and terephthalic resins and similar chemicals.

DYNASIL
Ethyl-ortho- and Ethyl-poly-silicates, Silicone-aluminium ester, suitable for the preparation of anti-corrosive lacquers.

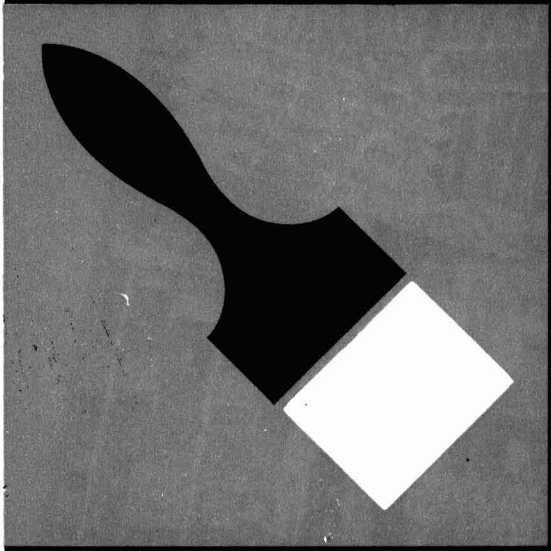
RHENOFLEX
Chlorinated Polyvinylchloride for the preparation of strippable coatings and anti-corrosive lacquers.

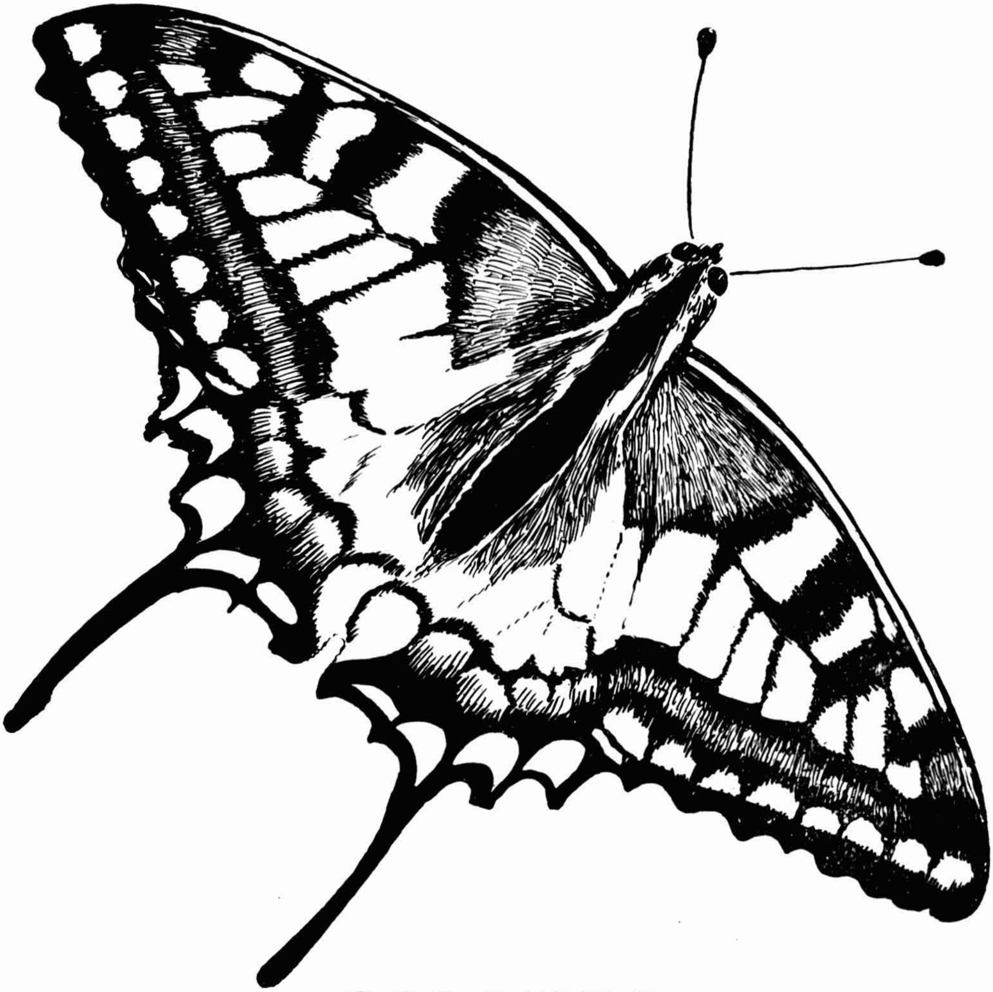
Kindly ask for detailed information.

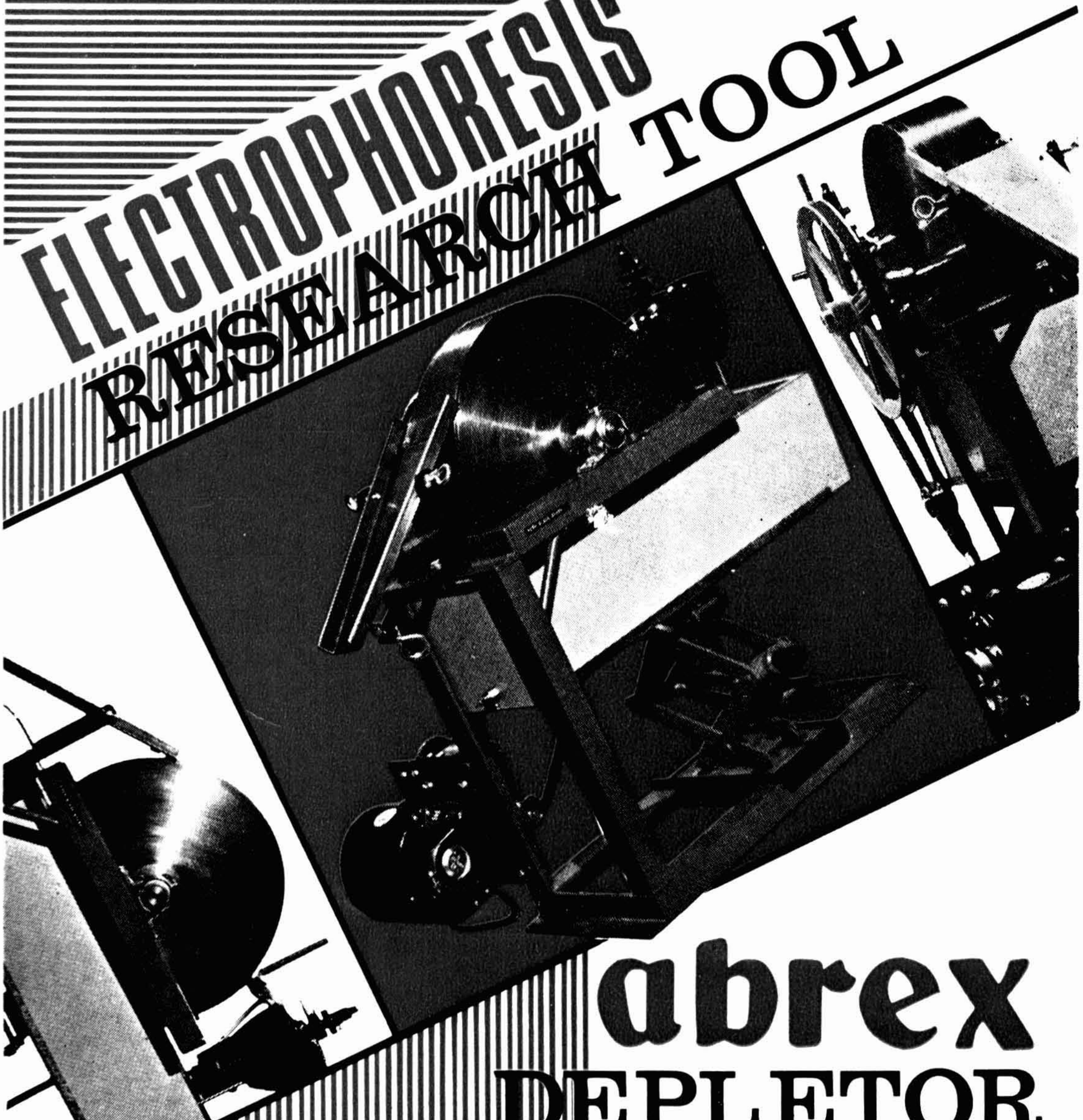
Dynamit Nobel, Vertrieb Chemikalien
5 Köln-Mülheim, Wiener Platz 4

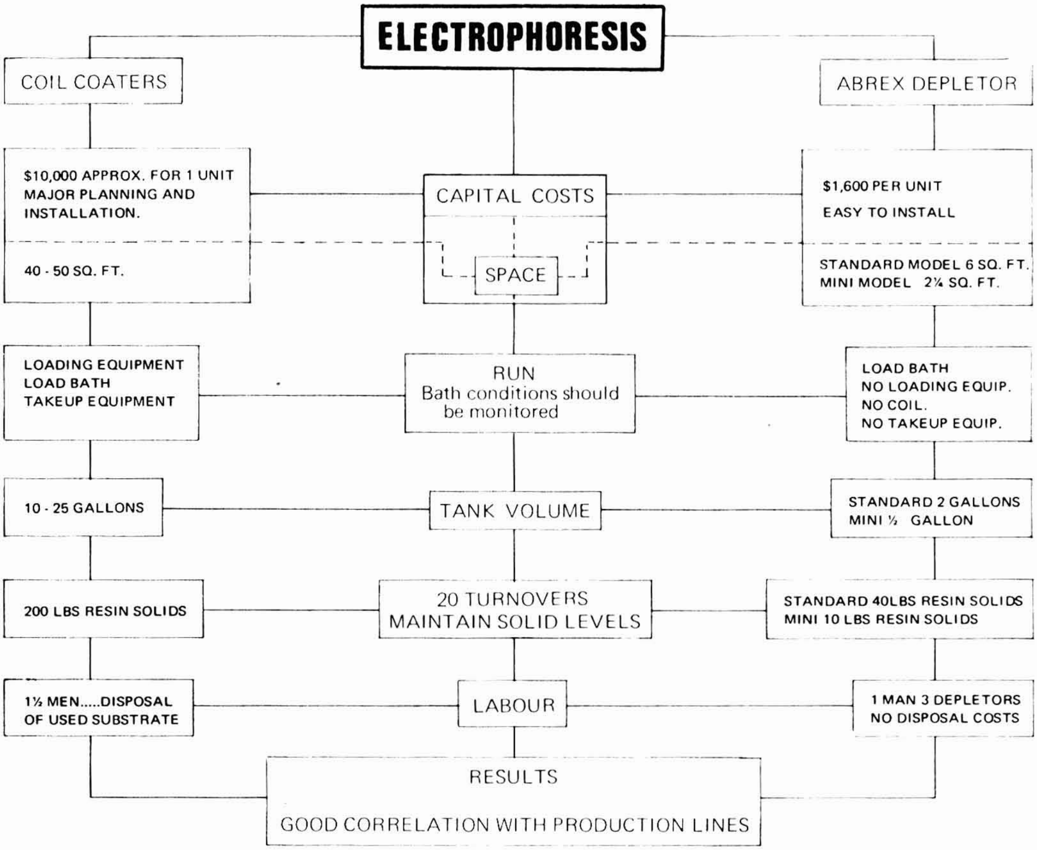
Dynamit Nobel
CHEMICALS

6908 e









It is essential to have a knowledge of how the paint bath composition changes during deposition through a number of depletion cycles, or turnovers, in order to be able to formulate a suitable feedstock or to devise a means of controlling the unwanted buildup of non-depositing ingredients. To observe the effect of depletion (with or without simultaneous replenishment) it is necessary to coat large areas of substrate. Usually this involves either the repeated laborious coating and stripping of a large number of metal panels, or the coating of a continuous strip which is then discarded as waste. Both methods are expensive.

The Abrex DEPLETOR is designed to overcome this problem. The submerged portion of the circumference of the flat-faced wheel is coated continuously, and the wet film after dragout removal by wiping, is continuously removed by a doctor blade, providing a fresh clean substrate surface for recoating. Suitable tests and analysis may be carried out on samples of the bath and of the "doctorate". Provision is made for recirculation, agitation and temperature control of the bath. Direct-current power for deposition is provided by a suitably-sized variable-voltage rectifier. For safety reasons, the wheel and all exposed metal parts of the Abrex DEPLETOR are at ground potential, and only the submerged cathode is at the potential selected by the operator.

It should be emphasized that the sole function of the Abrex DEPLETOR is to deplete an electrodeposition paint bath thereby simulating the bath conditions which occur on a production line. In other words, the Abrex DEPLETOR is not a testing device, as such, but a device for providing meaningful samples for testing. To anyone engaged in the development of organic coatings for electrodeposition, the Abrex DEPLETOR is an extremely useful, well-nigh indispensable, tool.

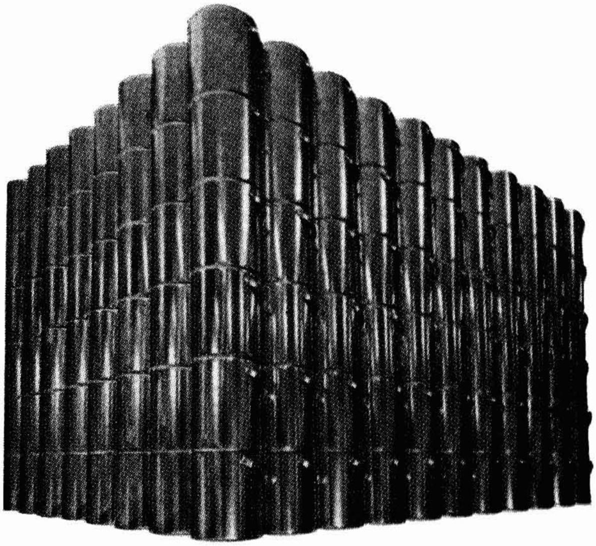
Depletor Specifications	Standard	Mini
Overall Dimensions	27"x30"x20"	12"x18"x10"
Weight	Approx 150lbs	Approx 25lbs
Tank Capacity	2+imperial gals	1+imperial qts.
Rectifier	0-250 volts D.C.	0-250 volts D.C.
Requirements	10 amps	5 amps
Price F.O.B. Oakville without Rectifier	$1,600 U.S.	$1,600 U.S.

ABREX SPECIALITY COATINGS LTD.

280 WYECROFT ROAD, OAKVILLE, ONTARIO, CANADA

A little Vinacryl styrene-acrylic binder

goes a long way

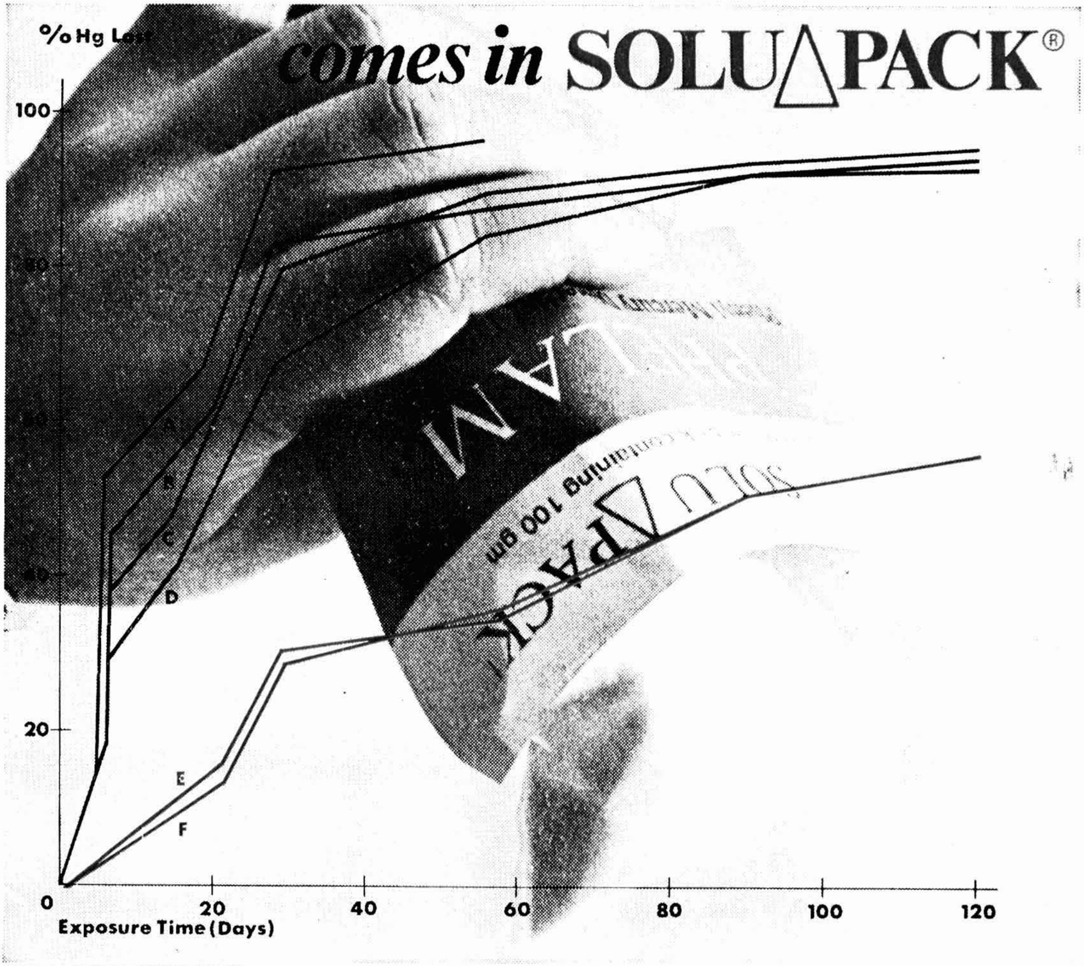


The ultra-high pigment binding power of Vinacryl 4172—good scrub resistance at 85% pigment volume concentration—helps you save money in interior paints: less emulsion, and more economical extenders, to a gallon of paint.

You can also prepare superbly durable exterior paints with low dirt pick-up, and excellent flexibility, proved by extensive weathering tests.

VINYL PRODUCTS LTD VP **Carshalton Surrey · 01-669 4422**

VP 141


%Hg Lost
100
80
60
40
20
0
A
B
C
D
E
F
20
40
60
80
100
120
Exposure Time (Days)
LAM
Containing 100 gm
SOLU∆PACK

INDEX TO ADVERTISERS

A

Abrex Specialty Coatings Ltd. .. .. .. vii, viii
Alliance Dye & Chemical Co. Ltd. i
Ashby, Morris, Ltd. xxxi
Associated Lead Manufacturers Ltd. xxix

B

Banner, Samuel, & Co. Ltd. xxx
Beadel, James, & Co. Ltd. xxxv
Beck Koller & Co. (England) Ltd. .. .. Cover
Berk Ltd. xii
BIP Chemicals Ltd. xxii
Bray, E. P., & Co. Ltd. vi
British Titan Products Co. Ltd. xiv

C

Ciba Clayton Ltd. xxvii
Chrispro Ltd. xix
Classified Advertisements .. .. xxxvi-xxxx
Cory, Horace, & Co. Ltd. xvi

D

Degussa Russe .. .. xxv, xxvi
Dynamit Nobel AG .. .. Cover

E

English China Clays Sales Ltd. ii

G

Geigy (UK) Ltd. xvii
Glovers Chemicals Ltd. xxiii
Golden Valley Colours Ltd. v
Greaves, Joshua, & Sons Ltd. xxviii

H

Henkel International GmbH iv

I

ICI Ltd. (Paints and Resins) iii
ICI Ltd. (Heavy Organics) xxi

M

Metchim & Son Ltd. xxxii
Mitchell, W. A., & Smith Ltd. ix

N

Nopco Hess Ltd. xxxiii

P

Peintures Pigments Vernis xxviii
Porter-Lancastrian Ltd. ix

R

Rhone-Poulenc .. .. Cover

S

SCC Colours Ltd. xi
Suter, A. F., & Co. Ltd. xxx

U

United Coke ; Chemical Co. Ltd. xxxii

V

Vinyl Products Ltd. x
Vuorikemia Oy xx

JOURNAL OF THE OIL & COLOUR CHEMISTS' ASSOCIATION

Vol. 52 No. 5 May 1969

MEMBER OF THE AUDIT BUREAU OF CIRCULATIONS

Publications Committee

Editorial correspondence should be addressed to the Hon. Editor, *JOCCA*, Cray Valley Products Ltd., St. Mary Cray, Kent.

General correspondence should be addressed to:

R. H. Hamblin, M.A., F.C.I.S., F.C.C.S.,
Director & Secretary,

Oil & Colour Chemists' Association,
Wax Chandlers' Hall, Gresham Street,
London, E.C.2 (Tel.: 01-606 1439).

Assistant Secretary: A. E. T. Collins, F.C.A.

Assistant Editor: R. Wood, B.SC.TECH.

Annual subscription to non-members in UK and abroad £7 10s post free, payable in advance. Single copies: 15s post free.


HUVENEERS
BTP
TITANIUM
PIGMENTS

JOURNAL of the OIL AND COLOUR CHEMISTS' ASSOCIATION

Contents **Vol. 52 No. 5** **May 1969**

Transactions and communications

Effect of inhibiting pigment in high-build chlorinated rubber systems for underwater use . . . . .
T. F. Birkenhead 383

The formulation of zinc oxide latex paints . .
E. Hoffmann and A. Saracz 393

Electron probe analysis in the investigation of surface coating problems . . . .
P. Whiteley, K. E. Fletcher and G. M. Rothwell 410

The influence of the solvent and of the substrate on the water vapour permeability of films . . . . .
R. Katz and B. F. Wunk 418

Review 433
Student review 434
Information received 457
Section proceedings 460
Register of members 468
Notes and news 468
Forthcoming events 489

Published by

OIL AND COLOUR CHEMISTS' ASSOCIATION
Wax Chandlers' Hall, Gresham Street, London EC2

J. Oil Col. Chem. Assoc. 1969, 52, 383-392

Transactions and Communications

Effect of inhibiting pigment in high-build chlorinated rubber systems for underwater use*

By T. F. Birkenhead

ICI Ltd., Mond Division, PO Box 13, Runcorn, Cheshire

Summary

A number of inhibiting pigments have been studied in high- and low-build chlorinated rubber primers by means of laboratory and raft tests. Preferred formulations are indicated.

Key words

Types and classes of coating
- rubber base coating
- rust inhibitive primer

Types of surface
- steel

Binders—resins etc.
- chlorinated rubber

Processes and methods primarily associated with analysis and testing
- sea water immersion test

Prime pigments
- aluminium pigment
- basic sulphate white lead
- lead pigment
- red iron oxide pigment
- red lead
- zinc dust

Chemically active pigments
- basic lead silicochromate
- calcium plumbate
- zinc chromate

L'effet du pigment inhibiteur dans des systèmes de haute teneur en matière sèche a base de caoutchouc chloré pour l'utilisation sous-marine

Résumé

On a étudié, par les essais laboratoires et sur radeau, une gamme de pigments inhibiteurs incorporés dans des primaires à caoutchouc chloré de haute et de faible teneurs en matière sèche. On mentionne les formulations ayant de bon rendement.

Der Einfluss Inhibierender Pigmente in Chlorkautschuk-Unterwasserfarben-Systemen Grosser Filmdicke

Zusammenfassung

Mit Hilfe von Laboratoriums- und Raft-Prüfungen wurde eine Anzahl inhibierender Pigmente in Chlorkautschukprimern von grosser und kleiner Filmdicke untersucht. Uber die ausgewählten geringer Rezepturen werden Angaben gemacht.

Влияние ингибирующего пигмента в высокоструктурных системах хлорированного каучука для подводного применения

Резюме

Изучался ряд ингибирующих пигментов в высоко– и низкоструктурных хлорированных каучуковых грунтовках путем лабораторных и плотовых испытаний. Указываются более предпочтительные формуляции.

---

*Presented to the London Section, Southern Branch, on 14 August 1968

Introduction

High-build chlorinated rubber systems are used today throughout the world for the protection of ships steel. Their ease of use, low temperature application, easy recoatability, one-pot system, together with excellent durability, have led to great interest in these systems by shipowners, shipbuilders and, of course, paint makers.

One of the factors currently being investigated in the author's laboratories is the effect of inhibiting pigment on performance of high-build systems. Two types of systems are being used.

1. Only the coat in contact with the bare steel or shop primer contains inhibiting pigment. This is overcoated with high-build coats based on inert pigments.
2. Each high-build coat contains inhibiting pigment, the so-called protection in depth.

Both systems are in use today and are giving good results; the second system has the merit of being simpler.

The work described in this paper covers both types.

Table 1

Effect of inhibiting pigment on primer performance in sea water immersion

Inhibiting pigment	PVC primer		Performance after 20 months' immersion (blistering)	
	Total	Active pigment	Menai Straits	Poole Harbour
Metallic lead I	32.4	8.2	Intact	Few—edge
Metallic lead II	38.2	8.1	Few—edge	Moderate—edge
Zinc metal	64.8	64.8	Intact	Few—edge
Aluminium	30	16.3	Intact	Intact
Basic lead sulphate	24.2	13.9	Moderate overall	Few—edge
Red lead	41	12	Moderate overall	Few overall
Red iron oxide	28.2	14.2	Few	Moderate overall
Calcium plumbate	28.4	14.9	Medium dense overall	Medium dense overall
Calcium plumbate*	30.1	13.2	Few	Moderate overall
Zinc chromate	28.8	15.2	Few	Few—edge
Zinc chromate*	31.5	22.1	Few—edge	Intact
Basic lead silicochromate . .	29.3	14.8	Few—edge	Few—edge
Basic lead silicochromate* . .	27.9	18.0	Slight—edge	Intact
No primer	—	—	Few overall	Few overall

All binders chlorinated rubber/chlorinated paraffin except those marked* which are similar binder modified with oil and alkyd.

Raft immersion trials

Sea water immersion tests from rafts in Menai Straits and Poole Harbour have been designed to show among other things, the effect of inhibiting pigment on primer performance. Thirteen chlorinated rubber primers were brush applied to grit blasted 18in × 24in panels (Sa 2.5 minimum). Film thickness was in each case about 1mil. These primers were then overcoated by airless spray with either two or three coats of chlorinated rubber high-build paints containing only inert pigments to give a total film thickness of either 9 or 13mil.

Observations made after 20 months' immersion are shown in Table 1.

They refer to the 9mil system; in general, better performance was obtained with the extra-high-build coat, i.e. the 13mil system, confirming the importance of thickness in underwater systems.

This experiment indicated the superiority of primers based on aluminium, metallic lead and zinc; the performance of the chromates was also good, perhaps unexpectedly.

In a further experiment, again conducted on the two rafts, the effect of inhibiting pigment on performance of high-build primers was studied. Three pigmentations were used: red lead, basic lead sulphate/aluminium/red iron oxide (as in BISRA 655[1]) and an extended aluminium. In addition vinyl, coal-tar epoxy and a chlorinated rubber control (low-build metallic lead primer/high-build coats containing only inert pigment) were also included. As well as pigment and binder type, this experiment studied the effect of surface preparation e.g. grit blast, shot blast, weld lines, flame cleaning, wire brushing and weathered shop primer.

The high-build chlorinated rubber primers were applied by airless spray directly on to bare steel or in some cases weathered shop primer. Three coats of each were applied to give a dry film thickness of 10-12mil total.

The formulations for the high-build primers are shown in Table 2. Formulation 2 is based on a composition developed by BISRA[1].

Table 2

Marine high-build coatings with inhibiting pigment for airless spray

Constituents	Composition by weight %		
	Red lead	Aluminium/ basic lead sulphate	Aluminium
"Alloprene" R10	12.1	12.3	12.0
"Cereclor" 42	4.0	4.1	4.0
"Cereclor" 70	7.1	7.2	7.0
NS Red lead	18.2	—	—
Spanish red oxide	18.2	6.7	—
Basic lead sulphate	—	13.3	—
Barytes	—	6.7	18.0
Non-leafing aluminium paste 65%	—	9.2	12.0
"Tioxide" R-CR	—	—	6.0
"Deanox" U90	—	—	1.0
Magnesium oxide	—	—	0.3
"Thixatrol" ST	1.6	1.6	1.6
Xylene	31.0	31.1	30.5
"Aromasol" H	7.8	7.8	7.6
PVC %	33.5	31.0	34.2
Wt./gall. lb	14.9	13.8	13.4

Apart from the shop primed panels, which had been allowed to weather for 3 or 9 months before overcoating, the panels have been immersed for 17 months; the results are indicated in Table 3.

Of the high-build primers studied, red lead is apparently the worst, with basic lead sulphate/aluminium marginally better than that containing only aluminium, but the experiment is as yet of insufficient duration to permit firm conclusions to be drawn. It is interesting to note that, at this early stage, the chlorinated rubber systems are performing better than those based on epoxy or vinyl resins.

Table 3

Effect of surface preparation and paint type immersion at Menai Straits for 17 months

Surface	Performance—blistering					
	"Alloprene" systems				coal tar epoxy†	vinyl‡
	red lead	aluminium	aluminium basic lead sulphate	control		
grit blast 16 mesh: Sa2 ..	few 1/10in	nil	nil	nil	nil	nil
grit blast 6-8 mesh: Sa2 ..	few 1/32in	nil	few 1/32in	nil	mod. 1/8in	med. dense 1/10in
cut/weld: grit blast: Sa2 ..	mod. 1/4in weld	nil	nil	few 1/10in	few 1/10in	few 1/10in
shot blast: shop primer:* weather 3 months ..	few micro	few micro	nil	nil	mod. micro	nil
shot blast: shop primer:* weather 9 months ..	few 1/16in	few 1/16in	nil	nil	few 1/32in	few 1/16in
pre rust: flame clean: brush	nil	nil	nil	nil	mod. 1/16in	nil

*Plates prepared at Cammell Laird, weathered in marine atmosphere, rust removed by light wire brushing plus fresh water wash, before overpainting.

†Average film thickness overall 8 mil.

‡Average film thickness overall 9 mil.

Optimisation of primer composition

The sea water immersion trials had shown that metallic lead and aluminium could give good results in chlorinated rubber systems. Paints of each type were tested in the laboratory to try to optimise formulations and improve performance.

Metallic lead

In the first experiment the factors investigated were:

(a) variation of lead PVC from 6-18 per cent with constant total PVC of 40 per cent (Microdol/Microtalc 3.2:1 by volume).

(b) variation of total PVC from 30-45 per cent, the level of lead varying from 9-13.5 per cent PVC (Microdol/Microtalc 3.2:1 by volume).

(c) variation in extenders keeping ratio of primary to secondary at 3.2:1.0 by volume at constant total PVC of 40 per cent and constant lead PVC of 12 per cent.

All the above paints had a common binder of 60:40 chlorinated rubber 20 cP/chlorinated paraffin 42.

(d) addition of drying oils to give binders of 60/30/10 and 70/20/10 of chlorinated rubber/chlorinated paraffin/oil.

The two lead primers referred to in Table 1 were used as controls.

Abraded mild steel panels were brush coated with the primers to give dry film thicknesses between 1.0 and 1.5mil. Half the panel was then overcoated with chlorinated rubber 20 cP/chlorinated paraffin 54 (60:40) white finish, pigmented with titanium dioxide at a PVC of 15.8 per cent.

A cut was made through to bare metal on the overcoated part. Panels were then subjected to salt spray, salt water soak and humidity for 500 hours, after which half the paint was removed for substrate examination.

Table 4 shows the performance rating.

Table 4

Performance rating (500 hours) low-build metallic lead primers

Primer			Salt spray	Humidity	Salt water soak	Total rating
Paint no.	Variable					
1	Lead	6.0	10	10B	8	28
2	Content	8.8	10	10B	8	28
3	Vol. conc.	12.0	10	10B	8.5	28.5
4	in %	14.8	10	10B	8	28
5		18.0	9.5	10B	6	25.5
6		30%	10	10B	6	26
7	PVC	35%	10	10B	6.5	26.5
3	Microdol/Microtalc AT1	40%	10	10B	8.5	28.5
8	3.2/1.0	45%	5.5	10B	5	20.5
9	Barytes/Microtalc		10	10B	9.5	29.5
10	Red/iron oxide/Microtalc		4.5	9.5	6	20
11	Microdol/Kiesulguhr		4.5	10B	6	20.5
12	Microdol/Asbestine		5.5	10B	7.5	23
13	Castor		9	9.5B	7.5	26
14	Blown castor		4.5	10B	7.5	22
15	Linseed		7	10B	7	24
16	Blown linseed		8	10B	7.5	25.5
Metallic lead I	see Table 1		5	10	2	17
Metallic lead II	see Table 1		0.5	0.5	2.5	3.5

B = Primer bleached. 10 = No corrosion. 0 = Severe corrosion (substrate).

The results show that:

increase in lead content has little effect up to a volume concentration of 14.8 per cent; higher concentrations than this cause deterioration (poor application properties may be a factor),

increase in PVC up to 40 per cent results in an increase in performance, but thereafter performance decreases,

barytes was the best primary extender,

oil addition leads to deterioration of the primer, especially in resistance to salty environment; castor oil was the best,

the primer which performed best was paint 9 in Table 4; the complete formulation is given in Table 5.

The two metallic lead primers which had been used in the raft immersion tests performed badly in the laboratory tests; it is considered that this may be attributed to the extenders present—silica graphite (metallic lead I) and mica (metallic lead II).

Table 5

Metallic lead primer

Constituents	Composition % w/w
"Alloprene" R20	11.0
"Cereclor" 42	4.4
Microtalc AT1	4.1
Barytes	19.6
Metallic lead paste (91% in "Cereclor")	32.0
"Thixcin" E	0.36
"Aromasol" H 3 White spirit 1	28 54

A second series of tests was designed (making use of the information already obtained) in a 2^5 factorial design experiment. The variables studied were:

A	PVC lead	7.5 and 15.0 per cent
B	PVC talc	5.0 and 10.0 per cent
C	castor oil	present and absent
D	PVC total	30 and 35 per cent
E	test method	salt water soak and salt spray

If the 16 higher order interactions are taken as a measure of error there were no statistically significant differences between the 32 panels. Alternatively, some of the higher order interactions may be real e.g. ABCD and ACDE. As this is technically possible the following conclusions may be drawn:

level of lead has no effect,
castor oil lowers performance,
total pvc level has no effect,
salt water soak was the more severe test.

On this basis, the best paint was one similar to that given in Table 5, but with a lower lead level. Replication of this experiment is indicated to confirm this.

Aluminium

Both low- and high-build coatings containing aluminium were examined; the factors investigated with the low-build primers were:

(a) total PVC 18-40 per cent,
(b) aluminium PVC 18-30 per cent using barytes as extender,
(c) addition of zinc chromate 0.7 per cent PVC,
(d) stabilisers: either zinc oxide or epoxidised soya bean oil (5 per cent of chlorinated rubber content) both with propylene oxide (0.5 per cent of chlorinated rubber content),
(e) binder: ratio chlorinated rubber to chlorinated paraffin either 70:30 or 60:40.

Panels were prepared in the same way as those for the experiments with metallic lead primers. The same three test methods were used but exposure periods were in some cases longer.

Table 6 summarises the test results.

Table 6

Performance rating of low-build aluminium primers

Paint no.	Primer		Salt spray 1,300hr.	Humidity 500hr.	Salt water immersion 1,300hr.	Total rating
	Variable					
1	PVC aluminium	18%	9	7	9	25
2	No extender	24%	8	8	9	25
5		30%	5	7	7	19
3	Increasing aluminium	60%	6	6	6	18
4	Total PVC constant at 30%	80%	7	7	9	23
5		100%	6	7	7	19
2	Total PVC	24%	8	8	9	25
4	PVC Al constant at 24%	30%	7	7	9	23
6		40%	2	4	7	13
3	Total PVC	30%	6	6	6	18
6	Al constant at 6% vol. of pigment	40%	2	4	7	13
7		50%	1	3	6	10
3	No zinc chromate		6	6	6	18
10	Zinc chromate 0.7% PVC		3	8	9	20
3	with ZnO stabiliser		6	6	6	18
4			7	7	9	23
5			5	7	7	19
12	with epoxidised soya bean oil		5	7	7	19
13			6	6	9	21
14			3	5	5	13
3	60/40 plasticisation		6	6	6	18
11	70/30 ,,		8	6	8	22

10 = No corrosion. 0 = Severe corrosion (substrate).

The results in Table 6 show that:

unextended aluminium is best, but that as PVC increased so performance decreased, owing probably to a worsening in brushability,

the addition of zinc chromate improves performance,

the 70:30 was slightly better than the 60:40 binder, possibly owing to the fact that water vapour permeability reduces as plasticiser content reduces,

the performance of the three paints containing the epoxy stabiliser was somewhat inferior to similar paints with zinc oxide as stabiliser; in addition, work on the gelation of chlorinated rubber/aluminium paints has shown zinc oxide to be the better stabiliser.

Table 7 gives a formulation for a conventional-build aluminium primer embodying most of the points brought out by the laboratory work.

Table 7

Aluminium primer: conventional-build

Constituents	Composition % w/w
"Alloprene" R20	18.7
"Cereclor" 42	8.0
Aluminium paste 65% non-leafing ..	24.2
Zinc oxide	0.9
"Aromasol" H	48.2

Although the raft immersion tests of the high-build primers given in Table 2 are of insufficient duration to enable firm conclusions to be reached, laboratory evaluation of variants of two of the formulations (aluminium, aluminium with basic lead sulphate) was considered desirable. The factors studied were:

(a) total PVC,

(b) thixotropic agent—hydrogenated castor oil (1.6 per cent on paint) or modified bentonite (3 per cent on paint),

(c) stabiliser—zinc oxide or magnesium oxide/iron oxide 3:1.

The paints were applied by airless spray to abraded mild steel panels to give, in one coat, 3mil dry film thickness. The test methods used were as for the low-build paints, but for a duration of 800 or more hours. The test results are summarised in Table 8.

The data in Table 8 shows that:

the aluminium paint was at about the optimum PVC, whereas the aluminium/basic lead sulphate could usefully be increased from 31 to 35 per cent,

hydrogenated castor oil was better than a modified bentonite,

the paint stabilised with zinc oxide was somewhat inferior to that stabilised with magnesium oxide/iron oxide; this may be explained by the fact that the level of zinc oxide, at 0.6 per cent on paint, was higher than that of magnesium oxide, at 0.3 per cent on paint, and both these pigments are water soluble.

Table 8

Paint no.	Thick coating	Salt spray 800hr	Humidity 800hr	Salt water immersion 800hr	Total rating
	Variable				
1	34.2%	10	9	10	29
2	Total PVC % 40%	10	7	10	27
3	Aluminium high-build primer* 45%	8	3	6	17
4	50%	9	3	9	21
5†	Total PVC % 30.8%	10	4	4	18
6†	Aluminium with basic lead sulphate high-build primer‡ 35%	10	9	10	29
7†	40%	10	7	10	27
1	Modified hydrogenated castor oil	10	9	10	29
14	Modified bentonite	7	4	10	21
1	Magnesium oxide/iron oxide	10	9	10	29
13	Zinc oxide	10	4	9	23

10 = No corrosion. 0 = Severe corrosion (substrate).

*see Table 2, third formulation.

†exposed for 1,500 hr.

‡see Table 2, second formulation.

Table 9 gives a formulation for a high-build primer based on aluminium with basic lead sulphate at the higher (35 per cent), preferred pigment volume concentration.

It is interesting to note that the presence of basic lead sulphate in the formulation in Table 9 makes addition of zinc oxide stabiliser unnecessary.

Table 9

Aluminium/basic lead sulphate primer: high-build

Constituents	Composition % w/w
“Alloprene” R10	12.0
“Cereclor” 42	3.9
“Cereclor” 70	6.8
Spanish red oxide	7.7
Basic lead sulphate	15.2
Barytes RS	7.7
Aluminium paste 65% non-leafing	10.5
“Thixatrol” ST	1.5
Xylene 4 “Aromasol” H 1	34.7

Conclusions

Sea water immersion and laboratory tests have been used to optimise primers, both low- and high-build, for use in chlorinated rubber high-build systems for underwater use. Formulations have been developed for low-build primers based on metallic lead or aluminium, and for high-build primers based on aluminium or aluminium with basic lead sulphate. Where the system required calls for a low-build primer, metallic lead extended with barytes/microtalc or unextended aluminium is preferred; for high-build primers, aluminium or aluminium with basic lead sulphate is preferred.

[*Received 31 December 1968*

Reference

1. "The Formulation of Anti-Corrosive Composition for Ship's Bottoms and Underwater Use on Steel." First Report of Joint Technical Panel N-P2. 1950: British Iron and Steel Research Association.

J. Oil Col. Chem. Assoc. 1969, 52, 393-409

The formulation of zinc oxide latex paints*

By E. Hoffmann and A. Saracz

Division of Building Research, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

Summary

An investigation has been made of the suitability of various latices for the formulation of latex paints containing large quantities (40 per cent by weight on total solids) of zinc oxide. Vinyl acetate-acrylic copolymer latices are the easiest to compound, but pva and pure acrylic copolymer latices, generally thought impossible to formulate, can be prepared if calcium silicate is used as an additive.

The conclusion is reached that it is likely that all types of latices could be used for the formulation of zinc oxide paints, provided that they have a low enough content of unreacted monomers and low molecular polymers.

It has also been shown that addition of barium metaborate to latex paints increases the viscosity, and this could be used to raise the consistency of paints which have thinned during storage.

Key words

Types of coating
latex paint

Prime pigments
titanium dioxide
zinc oxide

Chemically active pigments
barium metaborate

Binders—resins etc
acrylic resin
copolymer resin
vinyl acetate resin

Solvents
butyl ester

Extender pigments
calcium silicate

Plasticisers
dibutyl phthalate
tritolyl phosphate

Apparatus primarily associated with analysis and testing
viscometer

La mise au point des formules de peintures-émulsions à l'oxyde de zinc

Résumé

On a investigé l'aptitude de divers latices pour la préparation de peintures-émulsions contenant de grandes quantités (40 pour cent par poids de la totale matière sèche), de l'oxyde de zinc. Les latices-copolymères de l'acétate vinylique/acrylique se démontrent les plus faciles au point de vue de la fabrication de la peinture, mais d'ailleurs les latices de l'acétate polyvinylique et les latices-copolymères entièrement acryliques, en principe considérés impossible à s'en servir dans cette manière, peuvent être utilisés à mesure qu'on emploie le silicate de calcium en tant qu'adjuvant.

On conclut que tous les types de latices peuvent être utilisés dans la préparation des peintures-émulsions à l'oxyde de zinc dans le cas où la teneur en monomères non-réagis ou en polymères de bas poids moléculaire soient assez faibles.

D'ailleurs, on a démontré que l'addition de métaborate de baryum aux peintures-émulsions augmente-elle la viscosité. On pourrait utiliser cette caractéristique pour ameliorer la consistance des peintures qui ont devenues moins épaisses pendant le stockage.

---

*Presented to the Victorian section of the Oil and Colour Chemists' Association Australia, September, 1968.

Die Rezeptur für Zinkoxid-Latexfarben

Zusammenfassung

Die Eignung verschiedener Latexe für Rezepturen von Dispersionsfarben mit hohen Gehalten an Zinkoxid (40 Gewichtsprozent des Gesamtfestgehaltes) wurde geprüft. Am leichtesten lassen sich Vinylazetat-Akryl-Mischpolymerlatexe pigmentieren; PVA- und reine Akrylmischpolymerlatexe, von denen im allgemeinen angenommen wurde, dass ihre Verwendung nicht möglich sei, können, sofern zusätzlich Kalziumsilikat eingesetzt wird, hergestellt werden. Man kommt zu dem Schluss, dass wahrscheinlich alle Arten von Latexen für die Rezeptur von Zinkoxidfarben benutzt werden können, vorausgesetzt, dass ihr Gehalt an unreagierten Monomeren und niedrigmolekularen Polymeren gering genug ist.

Ferner wird gezeigt, dass Zusatz von Bariummetaborat zu Latexfarben die Viskosität erhöht. Diese Eigenschaft könnte dazu benutzt werden, um die Konsistenz von Farben, die beim Lagern dünner geworden war, zu erhöhen.

Формуляция латексоподобных красок на основе окиси цинка

Резюме

Изучалась применимость различных решеток для формуляции латексоподобных красок содержащих значительные количества (40 процентов твердых частиц по весу) окиси цинка. Винило-ацетатные акриловые сополимерные решетки наиболее легко подвергаются соединению, но поливиниловые ацетатные и чистые акриловые сополимерные решетки, которых обычно считается невозможным формулировать, могут быть приготовлены если применяется силикат кальция в качестве примеси.

Выводится заключение, что возможно что все типы решеток могут применяться для формуляции красок содержащих окись цинка, если они обладают достаточно низким содержанием нереагированных мономеров и низших полимеров.

Показано также, что добавка метабората бария к латексоподобным краскам повышает вязкость и этот факт может быть использован для увеличения плотности красок разреженных во время хранения.

Introduction

The authors have shown that latex paints containing zinc oxide (3.5lb per gallon or approximately 40 per cent by weight on the non-volatile matter of the paint) have a considerably higher fungus resistance than those without it[1,2]. However, these paints are very unstable and tend to solidify in the can, and it is therefore important to investigate the formulation of these coatings.

Published results on the preparation of zinc oxide latex paints are incomplete. Crouse[3] approached the formulation of these paints from a fundamental point of view by measuring the interaction of zinc oxide with some typical components of water thinnable paints. The studies involved examination of changes of dielectric effect with time and temperature, and sedimentation time of the suspended zinc oxide, but he did not show what use could be made of his data for the actual formulation of zinc oxide latex paints.

The effect of some zinc oxide pigments on the storage stability of paints is discussed in an information sheet issued by the Imperial Smelting Corporation[4]. It was found that incorporation of zinc sulphide or lithopone gave increased stability over a period of six months, and that zinc oxide made by the direct process proved to be the most suitable of those examined.

Munk[5] recommended the addition of a phosphate as stabiliser to the formulation, but he did not give any experimental justification for his claims.

The Electrolytic Zinc Co. of Australasia Ltd. has published a pamphlet with suggested formulations of latex paints containing zinc oxide pigment. The stability of these paints was followed for only three months at 20°C and for about one month at 49°C and no indication was given of their behaviour on prolonged storage.

The number of variables which presumably could influence the stability of latex paints containing zinc oxide as pigment is very high. The type of zinc oxide, wetting and dispersing agents, and the various latices, all would have some bearing on the storage stability of the coatings. The matter is further complicated by the disinclination of latex manufacturers to disclose any details of their products, and this also applies to the manufacturers of additives used in the preparation of latex paints.

In such a situation it is best to start in an empirical way, and experiments were designed to provide answers to the following questions.

(a) Which types of latices available in Australia are suitable for the formulation of zinc oxide latex paints?

(b) Is there any difference in the storage stability of two paints of different pigment volume concentrations?

(c) Is there any difference in the stability of two paints formulated with zinc oxides made by the direct and indirect processes?

(d) What is the influence of various additives that tend to increase the pH of the latex paint?

(e) Is it possible, by measuring the trend of viscosity and pH values with time, to extrapolate from the state of a paint at a few weeks to its state in about two years?

(f) In what direction should further experiments be carried out?

Materials

Zinc oxides

A. Made by the indirect process; lead content under 0.05 per cent; grain size $<1\mu$; surface area (by nitrogen absorption) 4.6m^2 g^{-1}.

B. Made by the direct process; lead content about 1 per cent; grain size 1-3μ; surface area (by nitrogen absorption) 2.1m^2 g^{-1}.

Latices

A vinyl acetate/acrylic copolymer (85:15)
A vinyl acetate/butyl fumarate copolymer (82:18)
Acrylic latex (supplier 1)
Acrylic latex (supplier 2)
pva latex

Rutile titanium dioxide

A widely used grade

Paints

Paints were made up to 45 per cent pigment volume concentration, and, in the case of the vinyl acetate-acrylic copolymer latex, also to 22 per cent pigment volume concentration. The pigment pastes were made up with the same thickeners (hydroxy ethylcellulose) and a mixture of non-ionic and anionic surfactants in the proportions usually recommended. Further relevant information on the composition of the paints is included in the tables. The appropriate amount of latex was then added to the pigment paste while stirring.

Experimental procedure

The prepared paint was divided into four parts containing the following additives to raise the pH: part 1, nil; part 2, 4 oz/gal calcium silicate ($CaSiO_3$); part 3, 0.3 oz/gal potassium tetraphosphate (KTPP); part 4, 4 oz/gal barium metaborate (BaB_2O_4).

Each part was then divided into two halves and placed in half-pint resin-coated cans. One series of the cans was stored at 20°C and the other at 38°C.

The apparent viscosity of the paint samples was measured with a Brookfield viscometer at 20°C at the intervals stated in the tables. Before carrying out the measurements, the paint was shaken and then allowed to stand for 30 minutes. The viscosities were determined at various speeds of the spindle (0.5, 1, 2.5, 10, 20, 50, and 100rpm).

Discussion

The results of the experiments are summarised in Tables 1 to 6.

Table 1

Change of viscosity with time
(Brookfield, poises)

Speed (rpm)	1 day	1 month	3 months	6 months	12 months	18 months	22 months
0.5	760	300	260	220	220	180	160
1	420	170	140	120	120	100	100
2.5	200	80	78	60	60	52	48
5	116	48	40	36	38	30	28
10	71	34	26	23	24	19	18
20	44	22	16	15	16	12	12
50	25	13	10	9	10	8	7
100	16	10	7	6	7	6	5

Formulation: Vinyl acetate-acrylic copolymer; pigment, ZnO (A); PVC, 45 per cent; additive, barium metaborate; storage temperature, 38°C.

General remarks

In every case the pH value dropped during storage, irrespective of the stability of the paint. This was also the case with pigment pastes to which no latex had been added, although the drop was not so big. This is an interesting observation, because the pH of a suspension of zinc oxide and titanium dioxide in distilled water will rise from 7.6 after preparation to 8.6 in the course of a few weeks.

This decrease in the pH values does not appear to be connected with the zinc oxide, because the values also decrease in paints formulated with rutile titanium dioxide as pigment (Table 3, paint 3). The pH values of paints prepared with the additives ranged from 8.5 to more than 9, but those without additives were lower. No conclusion as to the stability of the paint can be drawn from the change of pH.

The change in viscosity of a paint does not give any clue as to its behaviour. It might be expected that paints which tend to solidify would show a steady increase in viscosity, and that it would be possible to extrapolate from this to the time at which solidification will occur, but this is not the case. For example, the viscosity of formulation 1, with calcium silicate as additive, at 20°C first decreases and then starts to increase after 10 months, and solidification occurs in from 12 to 18 months (Table 3). Another example is formulation 2 (barium metaborate as additive) at 38°C (Table 4). In this case the viscosity decreases in the first 3 months, but then starts to rise and the paint eventually solidifies.

It is therefore clear that it is impossible to extrapolate from an early observation of viscosities to the further behaviour of the paints.

Table 1 shows the viscosity of a vinyl acetate/acrylic copolymer paint at the various speeds of the spindle after different times of storage at 38°C. The viscosity decreases with the rate of shear and time, and changes at the different speeds are approximately proportional. There is no additional information to be gained by measuring the consistency at the various speeds, and in Tables 2-5 the viscosity at only one speed (20rpm) is recorded.

Paints stored at 38°C are more prone to become solid, as is to be expected. One useful generalisation would appear to be justified by the observations. A paint which does not, within 6 months, solidify, become lumpy, or form a sediment which is hard to disperse, will remain in good condition for 18 to 26 months at 20°C, this being the length of time the various formulations have been observed. If a paint is to be used in a temperate climate similar to that of Victoria*, it would be sufficient to observe the formulations for 6 months at about 40°C. If no solidification or lumpiness occurs in this time it is very likely that the shelf life of the paint will be not less than about two years. If the paint is to be used in a warmer climate a longer time of observation is indicated.

No general conclusion can be drawn concerning the effectiveness of the additives which were used in this investigation, and it is impossible to say that any one is better than the other. The effect depends on the type of latex.

---

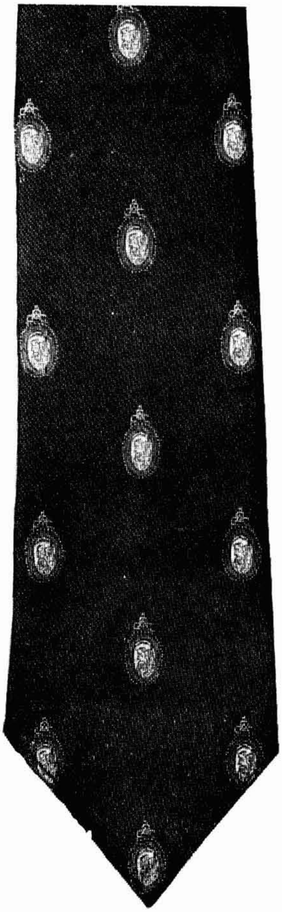
*In Melbourne the temperature exceeds 32.2°C on 20 days and 21.1°C on 120 days of the year, on an average.

Tabl

Experimental results—paints formulated on vin

Formulation	Additive	Stored at 20°C (68°F)								
		Viscosity Brookfield, Poise, 20rpm								
		1 day	1 month	3 months	6 months	10 months	12 months	18 months	22 months	26 months
1. Vinyl acetate/acrylic copolymer (85:15); 57% ZnO (B) (by weight on total solids).	Nil	8	9	16	25	25	24	20	17	17
	$CaSiO_3$	6	7	6	6	6	6	6	6	6
	KTPP	8	7	6	5	—	5	5	5	7
	BaB_2O_4	33	21	18	15	—	14	11	10	11
2. Vinyl acetate/acrylic copolymer (85:15); 57% ZnO (A) (by weight on total solids).	Nil	13	12	12	13	—	26	34	41	42
	$CaSiO_3$	10	10	9	9	—	9	8	8	8
	KTPP	13	12	10	10	—	10	9	9	11
	BaB_2O_4	44	32	25	21	—	20	16	15	16
3. Vinyl acetate/acrylic copolymer (85:15); 51% rutile TiO_2 (by weight on total solids).	Nil	12	11	10	10	10	10	9	9	9
	$CaSiO_3$	11	9	8	7	—	6	6	5	5
	KTPP	11	10	9	8	—	8	7	7	7
	BaB_2O_4	23	16	14	12	—	12	9	8	8
4. Vinyl acetate/acrylic copolymer (85:15); 30% ZnO (B) and 24% rutile TiO_2 (by weight on total solids)	Nil	9	9	8	6	9	10	10	12	13
	$CaSiO_3$	8	7	7	6	—	7	6	—	6
	KTPP	9	8	7	6	—	6	6	5	6
	BaB_2O_4	29	20	16	14	—	13	10	9	9
5. Vinyl acetate/acrylic copolymer (85:15); 30% ZnO (A) and 24% rutile TiO_2 (by weight on total solids).	Nil	11	11	10	12	—	14	14	14	15
	$CaSiO_3$	9	9	8	8	—	9	8	8	9
	KTPP	12	11	9	8	—	9	9	8	9
	BaB_2O_4	28	22	17	14	—	14	12	11	11

*Dispersion could be done only in shaking machine



The tie is blue terylene, with the Association's insignia woven in red and gold silk.

The blazer badge has the insignia embroidered in silver and gold wire on a red and blue ground.

The plaque has the insignia hand-painted in red and gold on a blue ground.

The car badge has the insignia embossed in red and gold on a blue ground, the whole being covered in transparent polypropylene, with a thick chrome surround. Bar and grille fittings are available.

In order to commemorate the Fiftieth Anniversary of OCCA, Council has authorised the production of a tie, blazer badge, wall plaque and car badge bearing the Association's insignia. These items are available only from :—

THRESHER & GLENNY

Lancaster Place, Strand,
London, W.C.2.

To : Thresher & Glenny Ltd., Lancaster Place, Strand, London, W.C.2.
As a member of the Association, please accept my order for the following:

......OCCA tie	@ 20/–	....	Name ....
......OCCA blazer badge	@ 63/–	....	
......OCCA wall plaque	@ 33/6	....	Section/No. ....
......OCCA car badge *(state bar or grille)*	@ 36/6	....	
			Address ....
(All prices include postage and packing)			....
If tie is required airmail add	6s. 6d.		....
Total Remitted			....

The ties will be supplied from stock; all other items are made to order. Only the tie can be supplied by airmail at an extra cost of 6s. 6d.

2

cetate/acrylic copolymer; PVC 22 per cent

Stored at 20°C (68°F)			Stored at 38°C (100°F)											
Interval in which paint became difficult to disperse* (months)	Interval in which paint solidified (months)	Range of pH values	Viscosity Brookfield, Poise, 20rpm									Interval in which paint became difficult to disperse* (months)	Interval in which paint solidified (months)	Range of pH values
			1 day	1 month	3 months	6 months	10 months	12 months	18 months	22 months	26 months			
—	—	8.1-7.1	8	25	19	14	12	10	8	8	7	—	—	8.1-6.8
—	—	8.3-7.6	6	10	S							—	1-3	8.3-8.0
—	—	8.4-7.3	8	7	16	18	15	16	11	11	10	—	—	8.4-7.0
—	—	8.9-8.0	33	16	15	14	—	14	10	10	10	—	—	8.9-7.5
—	—	8.5-7.1	13	15	38	34	—	30	22	19	17	—	—	8.5-6.7
—	—	8.6-7.8	10	9	9	S						—	3-6	8.6-7.9
—	—	8.8-7.4	13	11	11	19	—	31	50	25	23	—	—	8.8-7.1
—	—	9.1-8.0	44	22	11	15	—	16	12	12	12	—	—	9.1-7.6
—	—	8.2-6.9	12	11	13	14	14	14	12	12	12	—	—	8.2-6.3
—	—	8.5-7.6	11	9	8	7	6	6	6	6	5	—	—	8.5-7.2
—	—	8.4-7.1	11	9	8	7	—	7	5	4	10	—	—	8.4-7.0
—	—	8.9-7.8	23	13	11	9	—	9	7	7	6	—	—	8.4-7.3
—	—	8.2-7.1	9	11	19	18	16	15	16	21	18	—	—	8.2-7.1
—	—	8.5-7.6	8	9	13	14	13	14	11	11	10	—	—	8.5-7.2
—	—	8.4-7.2	9	7	7	9	—	16	13	11	12	—	—	8.4-6.9
—	—	8.9-8.0	29	14	12	10	—	11	8	6	6	—	—	8.9-7.5
—	—	8.5-7.2	11	15	17	20	—	21	8	7	7	—	—	8.5-7.5
—	—	8.8-7.5	9	10	12	14	—	14	12	11	11	—	—	8.8-7.3
—	—	8.9-7.3	12	10	9	13	S					—	6-12	8.9-7.4
—	—	9.1-7.9	28	15	11	10	—	9	17	16	16	—	—	9.1-7.0

S=sample solidified.

Tabl

Experimental results—paints formulated o

Formulation	Additive	Stored at 20°C (68°F)								
		Viscosity Brookfield, Poise, 20rpm								
		1 day	1 month	3 months	6 months	10 months	12 months	18 months	22 months	26 months
1. Vinyl acetate/acrylic copolymer (85:15); 80% ZnO (B) (by weight on total solids).	Nil	45	33	24	20	19	19	16	15	18
	$CaSiO_3$	26	21	18	15	15	20	S		
	KTPP	15	30	24	21	17	18	15	14	13
	BaB_2O_4	53	29	24	19	18	20	16	16	16
2. Vinyl acetate/acrylic copolymer (85:15); 80% ZnO (A) (by weight on total solids).	Nil	16	14	13	13	12	13	12	11	11
	$CaSiO_3$	13	12	11	11	10	11	9	9	8
	KTPP	16	15	13	12	11	12	12	11	10
	BaB_2O_4	38	27	22	20	18	20	20	18	18
3. Vinyl acetate/acrylic copolymer (85:15); 75% rutile TiO_2 (by weight on total solids).	Nil	24	20	19	20	20	22	22	22	23
	$CaSiO_3$	21	17	15	14	11	13	11	10	10
	KTPP	20	17	15	14	13	15	14	12	13
	BaB_2O_4	59	37	30	23	21	21	21	20	20
4. Vinyl acetate/acrylic copolymer (85:15); 44% ZnO (B) and 33% rutile TiO_2 (by weight on total solids).	Nil	13	17	18	18	20	20	20	21	22
	$CaSiO_3$	12	11	11	11	11	12	11	12	12
	KTPP	11	10	9	9	10	13	15	15	15
	BaB_2O_4	48	31	25	20	17	18	16	15	15
5. Vinyl acetate/acrylic copolymer (85:15); 44% ZnO (A) and 33% rutile TiO_2 (by weight on total solids).	Nil	18	16	16	17	21	22	19	19	20
	$CaSiO_3$	15	14	13	12	12	14	13	12	12
	KTPP	17	16	14	13	12	12	10	11	11
	BaB_2O_4	38	28	20	19	17	19	16	16	15

*Dispersion could be done only in shaking machine. S = sample solidifie

3

vinyl acetate/acrylic copolymer; PVC, 45 per cent

Stored at 20°C (68°F)			Stored at 38°C (100°F)											
Interval in which paint became difficult to disperse* (months)	Interval in which paint solidified (months)	Range of pH values	Viscosity Brookfield. Poise, 20rpm									Interval in which paint became difficult to disperse* (months)	Interval in which paint solidified (months)	Range of pH values
			1 day	1 month	3 months	6 months	10 months	12 months	18 months	22 months	26 months			
—	—	8.0-6.9	45	51	S							—	1-3	8.0-6.9
—	12—18	8.4-7.2	21	18	S							—	1-3	8.4-8.0
—	—	8.5-6.8	15	23	21	18	15	12	12			6-10	—	8.5-6.8
—	—	9.2-7.8	53	19	14	13	13	13	12	12	10	10-12	—	9.2-7.6
—	–	8.6-7.6	16	14	13	13	15	18	19	19	18	—	—	8.8-7.2
—	–	8.9-8.1	13	12	11	S						—	3-6	8.9-8.4
—	—	9.0-8.2	16	16	13	12	11	12	10	10	11	3-6	—	9.0-7.8
–	—	9.2-8.7	38	20	17	16	16	16	14	13	13	—	—	9.2-7.7
—	—	8.5-6.9	24	24	21	21	19	19	18	15	16	—	—	8.5-6.3
—	—	8.2-7.7	21	16	14	13	12	12	14	11	10	—	—	8.2-7.4
—	—	8.9-7.1	20	16	15	13	11	12	9	9	10	—	—	8.9-6.9
—	—	9.1-8.0	59	27	20	19	18	18	13	12	12	—	—	9.1-7.6
—	—	8.2-7.5	13	25	21	23	S					—	6-10	8.2-7.3
—	—	8.6-7.6	12	19	16	13	13	27	S			—	10-12	8.6-7.3
—	—	8.6-7.1	11	12	18	16	15	14	35	S		—	18-22	8.6-7.5
—	—	9.1-8.0	48	22	17	14	13	13	10	11	11	—	—	9.1-7.4
—	—	8.5-7.6	18	19	25	21	20	20	18	18	16	—	—	8.5-7.3
—	—	8.9-7.5	15	15	15	16	15	15	13	12	11	—	—	8.9-7.6
—	—	9.0-7.0	17	15	14	13	§					—	—	9.0-7.9
—	—	9.2-8.7	38	20	17	14	13	13	12	10	9	—	—	9.2-7.6

§=No sample available for further measurements.

Table

Experimental results—latex paints

Formulation	Additive	Stored at 20°C (68°F) Viscosity Brookfield, Poise, 20rpm						
		1 day	1 month	3 months	6 months	11 months	14 months	18 months
1. Pva with 15% tritolyl phosphate as plasticiser; 44% ZnO (A) and 33% rutile TiO_2 (by weight on total solids)	Nil	23	24	27	33	33	33	36
	$CaSiO_3$	18	17	17	18	16	15	17
	KTPP	18	18	20	26	S		
	BaB_2O_4	34	29	27	30	S		
2. Pva with 15% dibutyl phthalate as plasticiser; 44% ZnO (A) and 33% rutile TiO_2 (by weight on total solids)	Nil	13	17	18	20	22	—	21
	$CaSiO_3$	11	12	11	11	12	11	11
	KTPP	12	13	20	16	62	S	
	BaB_2O_4	27	23	20	22	21	25	48
3. Pva without plasticiser; 44% ZnO (A) and 33% rutile TiO_2 (by weight on total solids)	Nil	23	23	27	30	33	34	45
	$CaSiO_3$	20	21	20	22	19	17	21
	KTPP	21	22	20	23	22	26	36
	BaB_2O_4	46	42	38	39	34	32	38
4. Pva; pigment paste 63% solids by weight	Nil	37	37	50	74	100	S	
	$CaSiO_3$	28	29	32	34	33	30	35
	KTPP	36	38	40	40	45	41	55
	BaB_2O_4	55	56	56	57	57	52	59

*Dispersion could be done only in shaking machine.

4

with plasticiser; PVC, 45 per cent

Stored at 20°C (68°F)			Stored at 38°C (100°F)									
Interval in which paint became difficult to disperse* (months)	Interval in which paint solidified (months)	Range of pH values	Viscosity Brookfield, Poise, 20rpm							Interval in which paint became difficult to disperse* (months)	Interval in which paint solidified (months)	Range of pH values
			1 day	1 month	3 months	6 months	11 months	14 months	18 months			
—	—	7.9-7.4	23	26	S					—	1-3	7.9-7.4
—	—	8.8-8.3	18	17	15	14	20	12	12	—	—	8.8-7.3
—	6-11	8.2-7.0	18	20	S					—	1-3	8.2-7.8
—	6-11	8.9-8.6	34	23	23	S				—	3-6	8.9-8.3
—	—	7.9-7.2	13	19	21	24	25	22	20	6-11	—	7.9-7.0
—	—	8.7-8.4	11	13	12	11	11	10	9	—	—	8.7-7.9
—	11-14	8.5-7.8	12	14	S					—	1-3	8.5-7.9
—	—	8.9-8.4	27	19	17	19	S			—	6-11	8.9-0.0
—	—	8.2-7.1	23	25	36	36	59	53	69	—	—	8.2-7.1
—	—	9.0-8.2	20	20	19	17	15	12	13	—	—	
—	—	8.4-7.3	21	19	29	53	S			—	6-11	8.4-7.5
—	—	9.0-8.1	46	36	29	27	23	21	23	—	—	9.0-7.7
—	11-14	8.4-8.1	37	47	87	90	100	S		3-6	11-14	8.4-8.0
—	—	9.2-8.5	28	34	34	33	34	30	28	—	—	9.1-8.8
—	—	8.8-8.2	36	39	40	40	48	44	43	—	—	8.8-8.0
—	—	9.1-8.6	55	55	51	46	46	43	48	—	—	9.1-8.6

S=sample solidified.

Table

Experimental results—paints based

Formulation	Additive	Stored at 20°C (68°F)							
		Viscosity Brookfield, Poise. 20rpm							
		1 day	1 month	3 months	6 months	10 months	11 months	16 months	22 months
1. Vinyl acetate/fumarate ester copolymer (82:18); 44% of ZnO (A) and 33% rutile TiO_2 (by weight on total solids)	Nil	17	17	16	19	—	20	22	22
	$CaSiO_3$	12	12	12	—	—	12	13	17
	KTPP	14	13	13	—	—	24	27	34
	BaB_2O_4	19	17	14	14	—	13	11	11
		1 day	1 month	3 months	6 months	11 months	14 months	18 months	
2. Acrylic copolymer (supplier 1); 44% ZnO (A) and 33% rutile TiO_2 (by weight on total solids)	Nil	25	28	34	85	S			
	$CaSiO_3$	19	19	20	24	37	68	S	
	KTPP	33	35	33	35	36	35	37	
	BaB_2O_4	66	69	43	46	S			
3. Acrylic copolymer (supplier 2); 44% ZnO (A) and 33% rutile TiO_2 (by weight on total solids)	Nil	33	49	54	55	58	59	59	
	$CaSiO_3$	20	22	28	32	37	40	41	
	KTPP	30	33	41	47	57	59	62	
	BaB_2O_4	62	76	77	77	100	93	92	
4. Vinyl acetate/acrylic copolymer (85:15) with 2% monomer; 44% ZnO (A) and 33% rutile TiO_2 (by weight on total solids)	Nil	35	S						
	$CaSiO_3$	29	24	25	25	21	20	20	
	KTPP	34	S						
	BaB_2O_4	50	38	36	45	76	100	240	

*Dispersion could be done only in shaking machine.

5

on various latices; PVC, 45 per cent

Stored at 20°C (68°F)			Stored at 38°C (100°F)											
Interval in which paint became difficult to disperse* (months)	Interval in which paint solidified (months)	Range of pH values	Viscosity Brookfield, Poise, 20rpm								Interval in which paint became difficult to disperse*	Interval in which paint solidified	Range of pH values
			1 day	1 month	3 months	6 months	10 months	11 months	16 months	22 months			
<1	—	7.7-7.0	17	17	23	S					1-3	3-6	7.7-7.1
1-3	—	8.4-7.4	12	12	27	S					—	3-6	8.4-7.5
1-3	—	8.6-7.1	14	13	29	S					<1	3-6	8.6-7.2
6-11	—	8.5-7.8	19	13	14	S					1-3	3-6	8.5-8.0
			1 day	1 month	3 months	6 months	11 months	14 months	18 months				
3-6	6-11	8.4-8.1	25	48	S						<1	1-3	8.4-8.1
6-11	14-18	8.5-8.3	19	22	46	S					1-3	3-6	8.5-8.3
—	—	8.4-8.1	33	33	29	26	95	S			6-11	11-14	8.9-8.4
—	6-11	9.3-8.1	66	S							—	<1	—
—	—	8.5-8.2	33	57	51	43	39	40	S		6-11	14-18	8.5-8.2
—	—	8.9-8.5	20	37	39	36	34	28	S		—	14-18	8.9-8.5
—	—	8.9-8.1	30	51	58	52	55	43	S		11-14	14-18	8.9-8.3
11-14	—	9.3-9.0	62	100	S						—	1-3	9.3-9.0
—	<1	7.1	35	S							—	<1	7.1
—	—	7.8-7.6	29	21	46	S					—	3-6	7.8
—	<1	7.3	34	S							—	<1	7.3
—	—	8.6-7.4	50	100	S						—	1-3	8.6

S=sample solidified.

Table 6

*Effect of barium metaborate on viscosity of a latex paint**

rpm	Viscosity Brookfield, Poise, 20rpm	
	No Additive	With BaB_2O_4
0.5	100	340
1	60	180
2.5	32	80
5	14	44
10	10	26
20	9	15
50	5	9
100	3	6

*Rutile titanium dioxide pigment.

Barium metaborate is worth a special mention because it increases the viscosity of the paint in each case above that of paints without any additive or containing one of the others. For instance, formulation 2 (KTPP as additive), Table 2, has a viscosity of 13 poises and, with barium metaborate as additive, the viscosity is increased to 44 poises. However, on storage, the paints become thinner and, usually after about one year, the consistency of the paint is very near to that of the other coatings.

This property of barium metaborate could have a useful application. If a latex paint becomes too thin, the viscosity can be increased simply by adding barium metaborate at the rate of 4oz/gal. For example, a latex paint containing rutile titanium dioxide only had the viscosities before and after addition of barium metaborateas shown in Table 6. Whether this treatment is effective generally with all latex paints is impossible to say, since the mechanism of the increase and subsequent decrease in consistency is not known, but it was successful in those cases in which it was tried. Paints already containing barium metaborate are not susceptible to this treatment.

Behaviour of the various latices

Vinyl acetate/acrylic copolymer

Paints prepared with a vinyl acetate/acrylic copolymer latex are more stable than those prepared with the other latices. At 22 per cent PVC, with one exception, all paints containing a mixture of zinc oxide and rutile titanium dioxide were stable at the higher storage temperature for a period exceeding 26 months

(Table 2). The exception (formulation 5 with KTPP as additive) was usable for more than six months, and would be acceptable for use in a temperate climate.

Coatings containing zinc oxide pigment only and calcium silicate additive failed at the higher temperature, with solidification occurring in less than 6 months.

All paints stored at the lower temperature were in good condition after 26 months. No appreciable difference was found between paints containing zinc oxide A and zinc oxide B.

More failures occurred at 45 per cent PVC than at the lower level of PVC (Table 3), but all paints prepared with a mixture of zinc oxide and rutile titanium dioxide would be stable enough for use in a temperate climate. Of the paints prepared with zinc oxide pigments only, those formulated with zinc oxide A would appear to be somewhat more stable.

Pva latex (*Table 4*)

Of the paints prepared with tritolyl phosphate as a plasticiser (formulation 1), only the one with calcium silicate as an additive proved stable for more than 18 months at both storage temperatures.

Of the paints prepared with dibutyl phthalate (formulation 2), only the one formulated with calcium silicate was stable at the two storage temperatures for more than 18 months, but there was an improvement in the stability with this plasticiser. The coatings containing no additive or barium metaborate were stable enough for use in a temperate climate.

The stability of the paints to which no plasticiser had been added (formulation 3) was very satisfactory, and only one (KTPP as additive) was not stable for more than 18 months at 38°C. This formulation would be suitable for conditions in a temperate climate.

It is generally believed that pva paints cannot be formulated satisfactorily with a zinc oxide pigment, but this series of experiments shows that a stable coating can be obtained if calcium silicate is used as an additive. It is evident that the two compounds which have been used as plasticisers are really the cause of the difficulty, and it is possible that more stable paints could be prepared if a different type of compound were used as plasticiser.

Vinyl acetate/fumarate copolymer (*Table 5, formulation 1*)

None of the paints prepared with this latex was satisfactory.

Acrylic copolymers (*Table 5, formulations 2 and 3*)

Supplier 1: (50:50 ethyl acrylate: methyl methacrylate copolymer with small quantities of a third monomer). Only formulation 2 with KTPP as additive would be satisfactory for temperate conditions.

Supplier 2: (50:50 ethyl acrylate methyl methacrylate copolymer). Paints prepared with this latex were more stable than those obtained from supplier 1. Coating formulations 3 (no additive, calcium silicate and KTPP) were all usable.

It is widely believed that it is impossible to prepare acrylic paints containing large amounts of zinc oxide. Although coatings of this type are not as stable as those formulated with a vinyl acetate/acrylic copolymer, satisfactory paints for temperate conditions could be prepared.

Vinyl acetate/acrylic copolymer with 2 per cent monomer mixture added (Table 5, formulation 4)

Presence of the monomer in the latex leads to very unstable paints, but stable formulations can be obtained if no monomer is present (Tables 2 and 3).

This fact, and the observations made with the paints based on a pva latex, make it a reasonable working hypothesis that difficulties in preparing latex paints containing zinc oxide are due to esters, and if these are absent there should not be much difficulty in arriving at a satisfactory formulation.

The different behaviour of the various latices investigated could be due, to a significant degree, to small amounts of residual monomer or to the formation of low molecular weight polymers. An investigation in this direction could therefore be very fruitful.

Pigment dispersion (Table 4)

The pigment dispersion was made up with the same surface-active agents as the paints. It is of interest to note that only those dispersions which contained one of the additives were stable, whereas it is possible to prepare stable latex paints which do not contain any additive. It is difficult to explain this because the exact composition of the latices is not known. It is unlikely that any of the additives used in this work are added during the manufacture of the latices.

Conclusions

The following answers can be given to the questions asked in the beginning of the paper.

(a) The most suitable latex for the preparation of paints containing zinc oxide is a vinyl acetate/acrylic copolymer, but indications are that with the right type of additive, and provided that the latex has a minimum of free monomer and low molecular weight polymerisation products, this kind of paint can be formulated with every type of latex.

(b) Paints at a lower pigment volume concentration are somewhat more stable than those formulated at a higher concentration.

(c) The difference between zinc oxides made by the direct and indirect processes is negligible, but it should be emphasised that zinc oxide made by the direct process (B) should not be used because its lead content could give rise to sulphide staining. It should also be mentioned that zinc oxide B does not promote fungus resistance on outdoor exposure[6], but the effectiveness of this type in paints used indoors is not known.

(d) Additives like calcium silicate, potassium tetraphosphate, and barium metaborate have a characteristic influence on the stability of zinc oxide latex paints. For example, stable pva paints with tritolyl phosphate as plasticiser can be prepared only with calcium silicate as an additive.

(e) The trend of the viscosity and pH value over a comparatively short time does not allow the stability of the paint to be predicted after storage for two years or more.

(f) More detailed investigation of the influence of monomers and low molecular weight polymers would be very useful, and it would also be of use to test the stability of the paints stored at about 50°C. It is possible that this would reduce the time needed to assess the suitability of a given formulation.

As a further conclusion, it would appear to be a reasonable assumption that paints which are stable for more than 6 months at 40°C will be stable for about two years at the temperatures prevailing in temperate regions. Barium metaborate may be used to adjust the viscosity of paints which have fallen off in consistency. Approximately 4oz per gallon is sufficient for this purpose.

[*Received 31 December 1968*

References

1. Hoffmann, E., and Saracz, A., *JOCCA*, 1967, **50,** 425.
2. Saracz, A., and Hoffmann, E., *JOCCA*, 1968, **51,** 103.
3. Crouse, R. H., 11T Research Institute Technology Centre, Chicago, Ill., Report 1963 to 1964.
4. Imperial Smelting Corporation (NSC) Ltd., Technical Information No. P/2.
5. Munk, F., *Farbe und Lack*, 1962, **68,** 39.
6. Hoffmann, E., and Saracz, A., *JOCCA*, 1968, **51,** 921.

J. Oil Col. Chem. Assoc. 1969, **52**, 410-417

Electron probe analysis in the investigation of surface coating problems

By P. Whiteley, K. E. Fletcher and G. W. Rothwell

Building Research Station, Bucknalls Lane, Garston, Watford, Herts.

Summary

Applications of electron probe microanalysis in the surface coatings field are described. The technique, which combines elements of microscopy and chemical analysis, enables successive films to be differentiated, their thicknesses to be measured and certain constituents to be identified.

Key words

Types of surface	*Processes and methods primarily associated with analysis and testing*
aluminium	X-ray spectroscopy
masonry	
steel	
wood	

L'emploi de l'analyse à sonde électronique pour investiger des problèmes dans le domaine de revêtements

Résumé

On décrit quelques applications de la microanalyse à sonde électronique dans le domaine de revêtements. La technique, comprenant certains aspects de microscopie et d'analyse chimique, permet-elle de différencier les feuils consécutifs, de mesurer leur épaisseur et d'établir l'identité de certains constituants.

Elektronstrahlen-Spektroanalyse zur Erforschung von Anstrichproblemen

Zusammenfassung

Die Anwendung der Elektronstrahlen-Spektroanalyse auf das Anstrichmittelgebiet wird beschrieben. Mit Hilfe dieser Technik, in welcher Elemente der Mikroskopie mit denen der chemischen Analyse kombiniert werden, wird es möglich, übereinander liegende Filme zu unterscheiden, deren Dicke zu bestimmen und gewisse Bestandteile derselben zu identifizieren.

Пробный электронный анализ в исследовании проблем связанных с поверхностными покрытиями

Резюме

Описываются применения пробного электронного микроанализа в области поверхностных покрытий. Технология, объединяющая элементы микроскопии и химического анализа, позволяет различать последовательные пленки, измерять их толщину и опознавать некоторые компоненты.

Introduction

In many investigations of surface coatings on building materials it is necessary to know the thickness and sequence of paint coats and to have information about their constituents. The usual methods of microscopy, plus separation and analysis of applied films, can be time-consuming at all but the lowest degree of sensitivity. Using samples prepared as for microscopy,[1] electron probe microanalysis can give rapid information about the distribution of individual elements, plus a reflected electron image of the surface which has many of the characteristics of a normal microscope image.

Principles of electron probe analysis and experimental technique

Detailed descriptions of electron probe microanalysis can be found in text books[2,3], but an outline is give here since the technique is not yet in common use.

A beam of electrons is focused to a spot of about 1 μm^2 on the surface of the sample, causing the elements present in this region to emit their characteristic X-rays, which are diffracted by a crystal spectrometer and detected by an ionisation counter. The electron beam can be made to scan any selected area (up to about 1 mm^2 at lowest magnification) of a sample of size up to $80 \times 45 \times 10$mm thick. The electrons reflected from the surface can be used to form an image of the area on the screen of a cathode-ray tube, while simultaneously the distribution of particular elements within the area can be displayed on a second cathode-ray tube. Different elements are presented by selecting suitable angles of diffraction and each display is photographed separately. The instrument used in this work was the "Geoscan" electron probe X-ray microanalyser produced by the Cambridge Instrument Company Ltd. An excitation energy of 20 KeV was generally suitable for the investigations described. In the photographs of the displays the presence of a particular element is shown as white on a black background, and there is usually some slight background scatter. The density of the white area varies with the beam selected and the time of exposure, but in any single photograph is related to concentration. The method can be made quantitative by comparing the count rates with those given by a reference standard, but this is not easy with fine particles and with inhomogeneous materials. The lightest element which can be detected by this model of the instrument is sodium; elements which give useful information on surface coatings are: Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Fe, Cu, Zn, Sn, Sb, Ba, Pb. The method offers little help with paint media, since C, H, O and N, the predominant elements, could not be distinguished; however only the last two would offer much information.

The samples were mounted in a cold setting epoxy resin and ground so as to expose a cross-section of the coatings at right angles to the surface. A flat polished surface was produced by the methods used for optical microscopy, the final polishing being with a 0.25 micrometre diamond paste in oil. The surface was coated with a 300 Å carbon layer to conduct electrical energy away from the target area.

Results of typical investigations

Figs. 1 to 5 show the prints of analyses in five investigations; others have been unsuccessful and are described without illustrations to indicate limitations of the technique.

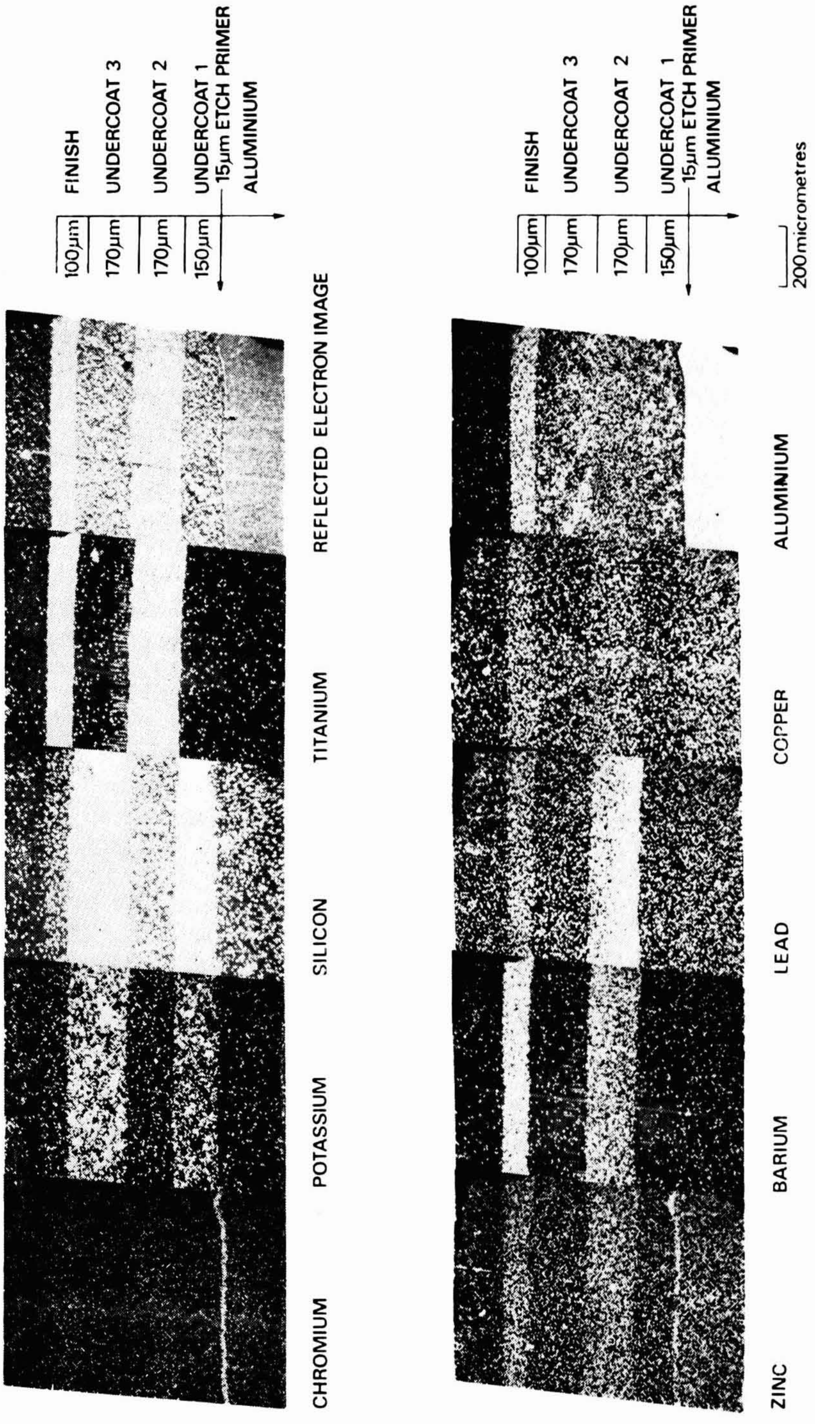


Fig. 1. Element distribution in a five coat protective system on aluminium

Protective system on aluminium cladding sheet

Interest centred on the priming treatment and the number, thickness and quality of the coats. Fig. 1 (top row) shows the reflected electron picture on the extreme right. Four principal coats were immediately evident, with indications of a thin film at the aluminium interface. The element distribution shown in the other photographs clearly indicates the thickness of all five coats (amounting to 600μm) and the individual pigmentations according to their main constituents. The initial thin layer contains zinc and chromium and is deduced to be an etch primer. In the intermediate coats the silicon, potassium and aluminium suggest the presence of extenders such as mica, talc or silica. Undercoats 1 and 3 appear similar, but undercoat 2 was distinguished by the presence of titanium, lead and barium. Some sulphur (no print shown) was detected in undercoat 2 and the finish coat. The presence of copper in the finishing coat was attributed to phthalocyanine blue for tinting.

Various pigment combinations could account for the elements present and it is not possible to distinguish them without further quantitative analysis or possibly full-scale X-ray diffraction. Thus, with titanium dioxide, probably alumina surface-treated, as the principal pigment, either barium sulphate and zinc oxide plus white lead or basic lead sulphate could be present, or less likely, lithopone. Optical microscopy and other tests established that the three intermediate coats had a bituminous (possibly with epoxy resin) basis.

Heavy duty bituminous coating on steel sheet

Fig. 2 illustrates an investigation primarily concerned with the undercoats and condition of the steel surface. The undercoating appeared to be mainly pigmented with a potassium aluminium silicate, possibly plus free silica. The top coat was largely a natural iron oxide containing alumina. The primer was deduced by optical microscopy and other tests to be a rather thin bituminous coat. At this magnification (each photograph representing about 0.1mm of coating width) there is a suggestion of differing density near the surface of the steel, suggesting the presence of scale or rust, but penetration of an iron oxide pigment would have been indistinguishable.

A four-coat system on a wooden window component

Fig. 3, a and b, shows two systems on different sections, illustrating the situation which can arise, by accident perhaps, when parts of the structure have been painted at different times. The four-coat system specified was to have included a lead-based pink primer, two coats of alkyd undercoat and one of alkyd gloss paint. A lead primer coat is shown in contact with the wood in Fig. 3a, but in Fig. 3b a non-lead coat is interposed. In Fig. 3a it is not possible to distinguish two separate undercoats, but the thickness would indicate two and this can be confirmed by reference to Fig. 3b. An incorrect sequence of coats is therefore clearly demonstrated. The top coat was abnormally thick at about 80μm. The penetration of the primer into the cells of the wood is very clearly shown by comparison of the reflected electron image and the photograph of the titanium distribution in Fig. 3b[4, 5].

Paint failure on wooden window component

Another successful use of the probe is shown in Fig. 4 where interest was again

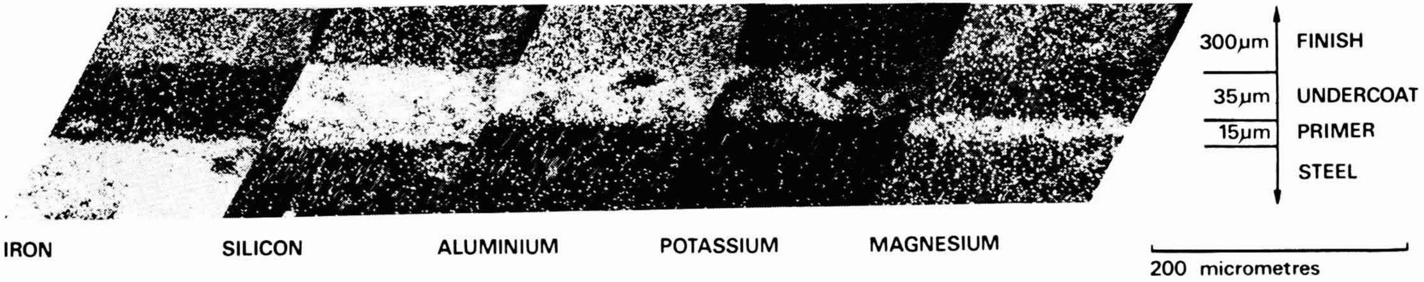


Fig. 2. Element distribution in a three coat protective system on steel

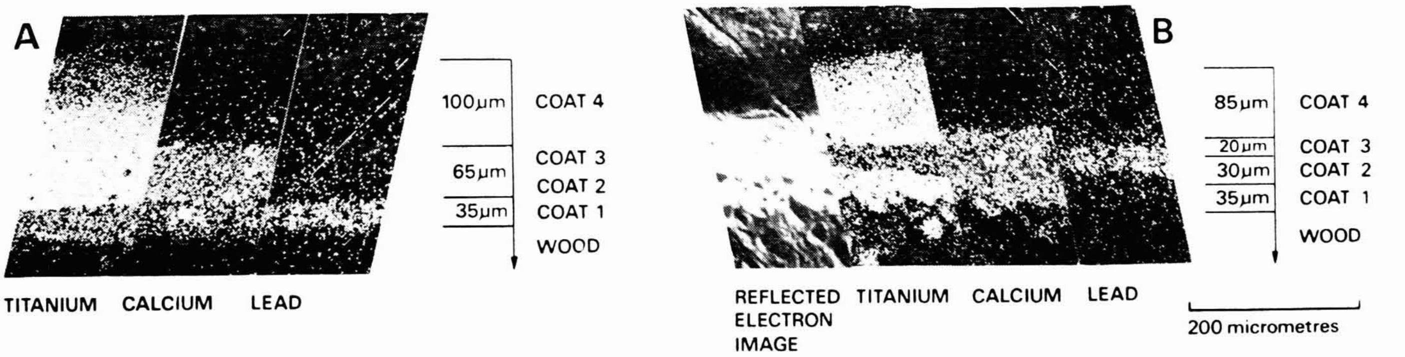
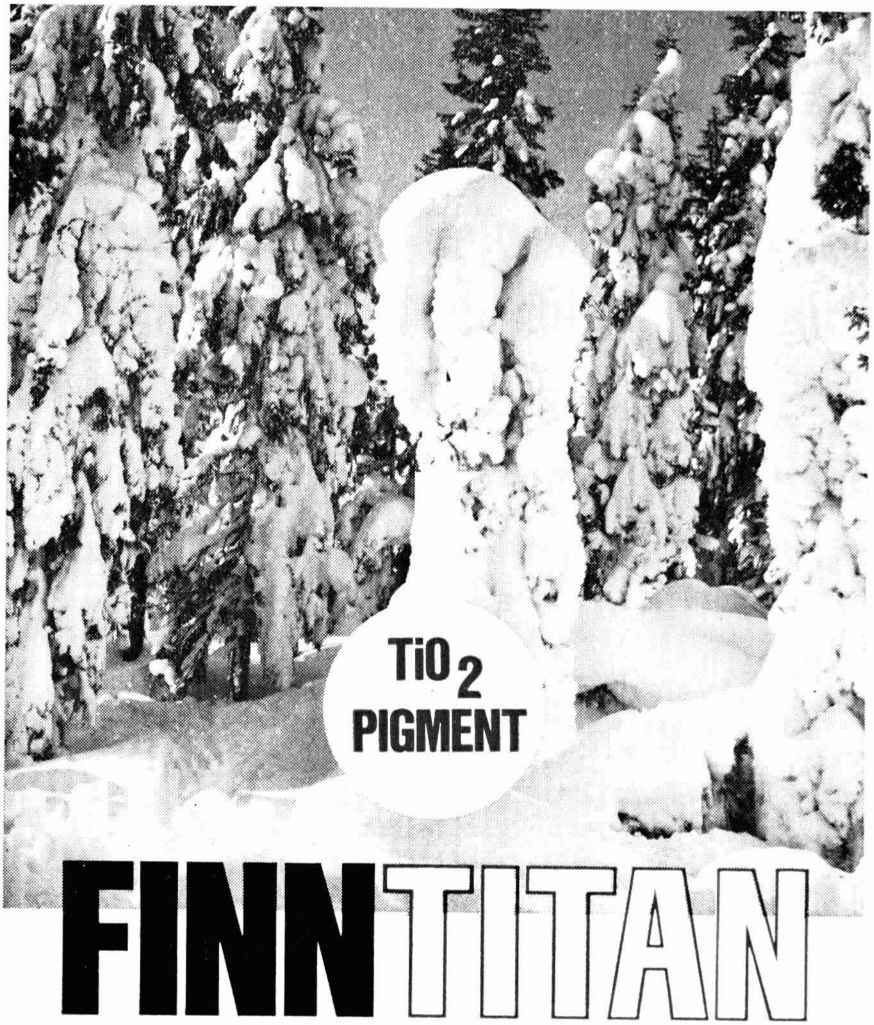


Fig. 3. Element distribution in four coat systems on wood


TiO2 PIGMENT
FINNTITAN

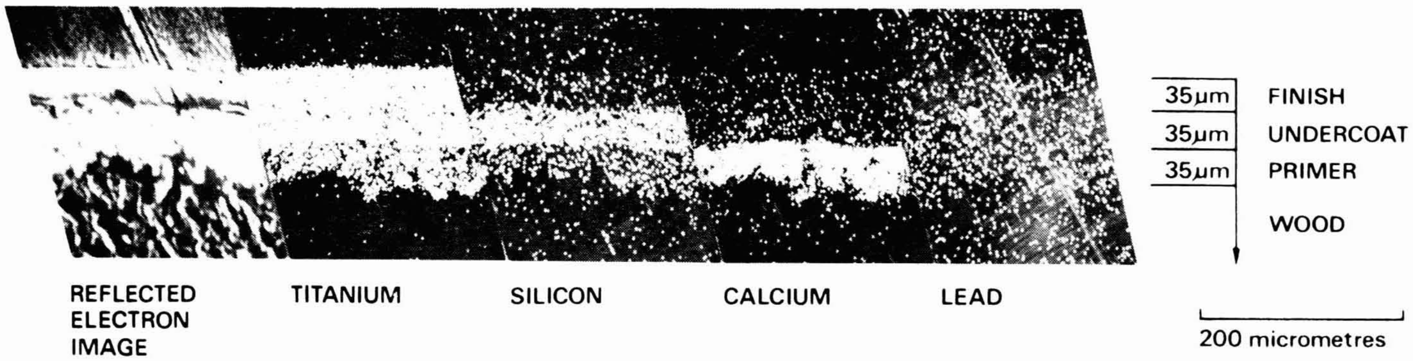


Fig. 4. Paint failure: Element distribution in a three coat system on wood

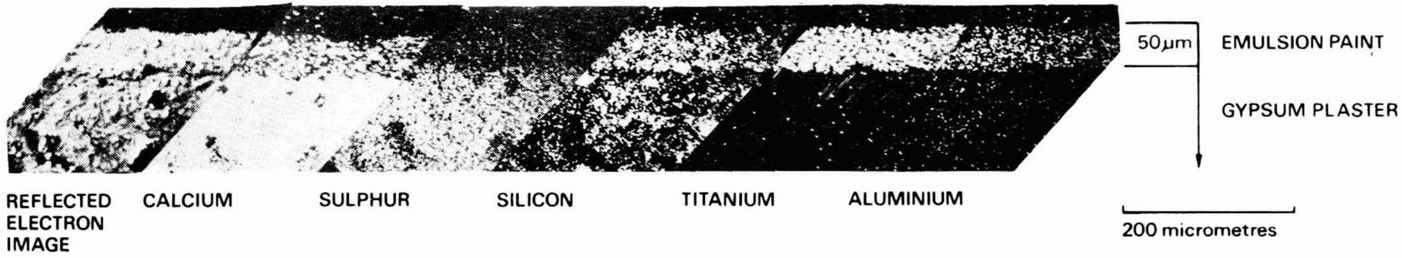


Fig. 5. Element distribution in emulsion paint on plaster

principally in the presence or absence of a lead-based primer and in the number, thickness and quality of following coats. Lead was shown to be present only at about the 1 per cent level. The primer contained a large concentration of calcium; the electron probe cannot identify this as carbonate but it was not sulphate or silicate. The undercoat contained silicon and aluminium. All three coats were rather thick. Other sections from the same work showed clearly the presence of only two coats, and optical microscopy indicated the primer to be both porous and chalky. The paint failure (flaking and mould growth) could be reasonably attributed to the use of an unsatisfactory primer, and omission of a coat in some areas, resulting in excessive water uptake.

Failure of emulsion paint on new plaster

The presence of calcium and sulphur shown in Fig. 5 indicates that the substrate was a gypsum plaster. The reflected electron image shows a weakness at the interface between the paint and plaster. The elements in the emulsion paint are typical but no differentiation into separate coats is possible. There is no evidence of a crystalline layer of efflorescence at the interface.

Inconclusive investigations

One field in which little success was achieved was an attempt to establish the presence of somewhat migratory constituents at low concentration in wood. Both pentachlorophenol and tributyl tin oxide contain elements detectable in other conditions by the electron probe, but were not shown to be present in treated wood. This was attributed partly to the low concentration and partly to a loss of these moderately volatile compounds during sample preparation and in the vacuum of the instrument.

The technique also failed to detect phosphorus in phosphate treatments on steel and zinc. The electron beam has a finite width of the micrometre order, and very thin coatings are at the limit of detection when the constituents are only in moderate concentration. Very thin coatings of zinc have been detected since the concentration was high and the element gives a strong X-ray signal. The phosphorus in a light or medium phosphate coating is only at low concentration in a layer of only 1 or 2μm thickness. Phosphorus, however, is usually detectable in steel.

In attempts to confirm claims that certain primers would penetrate rust on steel, the oil medium was loaded with lead (naphthenate) to give a detectable X-ray signal, but at a level of 0.5 per cent Pb on the paint no lead could be found. At a higher lead concentration (2 per cent) it could be detected and there was some evidence that it had penetrated into areas of rust where no other pigment was found, but not to the metal surface.

Conclusions

The ability of the electron probe to combine rapid elemental analysis with determinations of the film thickness and identification of coats offers a useful method for studying applied surface coatings, particularly for fault finding and confirmation or otherwise of adherence to a specification. The work illustrated here by no means exhausts the possibilities, and further refinement may offer a more quantitative result.

Acknowledgment

The work described here forms part of the Research Programme of the Building Research Station and is published by permission of the Director.

[Received 1 January 1969

References

1. Midgley, H. F., and Taylor, H. F. W., Chapter 20, vol. 2, Taylor, H. F. W. (Editor), "The Chemistry of Cements," 1964: Academic Press, London/New York.
2. Birks, L. S., "Electron probe microanalysis," 1963: Interscience Publishers, New York/London.
3. Adler, J., "X-ray Emission Spectroscopy in Geology," 1966: Elsevier Publishing Corporation, Amsterdam/London/New York.
4. Loon, J. van, *JOCCA*, 1966, **49,** 844.
5. Cote, W. A., Jr., and Robinson, R. G., *J. Paint. Tech*, 1968, **40,** 427.

J. Oil Col. Chem. Assoc. 1969, 52, 418-432

The influence of the solvent and of the substrate on the water vapour permeability of films

By R. Katz and B. F. Munk

Paint Research Association, Technion Campus, Haifa, Israel

Summary

Although much work has been carried out on the effect of various factors on the water vapour permeability of films, little is known about the influence of molecular orientation in film formation on permeability.

The orientation of molecules in a film could be influenced by the nature of the solvent or the substrate. Accordingly, unpigmented films of three polymers, nitrocellulose, chlorinated rubber, and an alkyd, have been cast from solvents of varying polarity on to several substrates, and the permeability measured.

It has been found that the polarity of the solvent has a definite influence on the permeability of the film. Only highly polar films, however, were influenced by the nature of the substrate.

Key words

Types of surface
- glass
- paper
- plastic
- tin foil

Types of coating
- alkyd coating
- rubber based coating
- nitrocellulose lacquer

Apparatus primarily associated with analysis and testing
- permeability cup

Properties primarily associated with dried or cured films
- water vapour permeability

L'influence exercée par le solvant et par le support sur la perméabilité de feuils à la vapeur d'eau

Résumé

Bien qu'on ait effectué beaucoup de recherches sur l'effet de divers facteurs sur la perméabilité de feuils à la vapeur d'eau, on n'a pas étudié en grand détail l'influence exercée sur la perméabilité par l'orientation moléculaire lors de la formation du feuil.

L'orientation des molécules du feuil pourrait être influencée par la nature du solvant ou du support. Ainsi on a déterminé la perméabilité des feuils a partir de trois polymères non-pigmentés, nitrocellulose, caoutchouc chloré et une alkyde, que l'on a coulé, en solvants de polarités différentes, sur plusieurs supports.

On a trouve que la polarité du solvant exerce une influence définie sur la perméabilité du feuil. Cependant la nature du support n'exerce qu'une influence importante dans le cas des feuils fortement polaires.

Der Einfluss des Lösungsmittels und des Substrates auf die Wasserdampfpermeabilität von Filmen

Zusammenfassung

Obgleich viele Arbeiten durchgeführt wurden, um den Einfluss verschiedener Faktoren fau die Wasserdampfpermeabilität von Filmen aufzuklären, ist wenig über den Einfluss molekularer Orientation bei der Filmbildung bekannt geworden.

Die Orientierung der Moleküle in einem Film könnte durch die Natur des Lösungsmittels oder des Substrates beeinflusst werden. Infolgedessen wurden unpigmentierte Filme dreier Polymerer, Nitrozellulose-, Chlorkautschuk- und ein Alkydharzlack, die in Lösungsmitteln verschiedener Polarität gelöst wurden, auf verschiedene Substrate aufgegossen und ihre Permeabilität gemessen.

Es wurde gefunden, dass die Polarität des Lösungsmittels die Permeabilität des Filmes entscheidend beeinflusst. Durch die Natur des Substrates wurden allerdings nur hochpolare Filme beeinflusst.

Влияние растворителя и субстрата на проницаемость водяных паров в пленках

Резюме

Хотя много работы посвящено изучению влияния различных факторов на проницаемость водяных паров в пленках, мало известно о влиянии молекулярной ориентации при образовании пленок, на проницаемость. Природа растворителя или субстрата может влиять на ориентацию молекул в пленке. Соответственно, непигментированные пленки трех полимеров, нитроцеллюлозы, хлоркаучука и алкида, осаждались из растворителей разной полярности на ряд субстратов, и измерялась их проницаемость.

Было обнаружено что полярность растворителя оказывает определенное влияние на проницаемость пленки. Природа субстрата, однако, оказывала влияние только на высокополярные пленки.

Introduction

Chemical and physical factors which alter the film structure, may influence also the water vapour permeability of the film.

Many papers[1–4] sum up the action of the following factors on water vapour permeability:

polar groups,
unsaturation,
symmetry,
lateral chains,
steric hindrance,
cross-links,
H-bonds,
intra-molecular forces,
copolymers,
crystallinity,
molecular weight,
plasticiser.

Far less is known about the possible influence of molecular orientation in film formation, which may be originated by the chemical affinity of the solvent, or by the surface activity of the substrate, or by both, on the film permeability.

The influence of solvent type

Payne[5] states that orientation of polymer molecules by solvent occurs, provided the solvent does not evaporate so rapidly that the molecules are immobilised before they can orient themselves in an organised film structure.

Differently oriented structures of the same polymer film may have different physical properties[15].

Ethyl cellulose films[6] deposited from toluene solution, have three times the elongation of similar films cast from ethanol solution. The tensile strength and water vapour permeability of the former films are also higher. Electron microscopy, X-ray diffraction, infra-red and ultra-violet measurements failed to show differences in the structure of the films. Yet mechanical and water vapour permeability tests point to some orientation of the film through solvent action, influencing different dimensional growth.

Working with nitrocellulose films cast from mixtures of acetone and propanol, Grabar[6] found that the pore size was controlled by the proportion of the two solvents in the mixture. The higher the acetone content, the less porous was the membrane. For nitrocellulose films[7] the highest water vapour permeability was that of films cast from acetone solution; this was less for ether:ethanol solution and lowest for solutions in esters.

Valle[8] used solutions of ethyl cellulose in benzene, chlorobenzene, 2-nitropropane, and mixtures of benzene with carbon tetrachloride. The highest tensile strength was measured in films cast from benzene/carbon tetrachloride mixtures, when stripped from glass. The differences disappeared when the films were formed by floating on mercury.

The influences of film-forming conditions on the properties of chlorinated low pressure polyethylene films were investigated by Kriston and Dimitrov[9–11]. The tear strength, the elastic modulus and the water vapour permeability values of polyethylene films cast from solutions in toluene, in chlorobenzene and in tetrachloroethane varied according to the solvent employed.

The influence of the substrate

It is a known fact that the presence of highly polar groups will improve the adhesion of certain coatings to smooth surfaces of metals[5], because of high affinity to the metal. For example, plasticisers, which are low molecular weight substances, are used for improving adhesion. These properties point to a possible mutual interaction between substrate and polymer and may suggest inhomogeneity in the film, caused by accumulation of polar groups and/or low molecular weight molecules at the metal coating interface.

Some evidence of substrate influence can be found in Valle's experiments[8] mentioned above: different tensile strength values were found for films stripped from glass or when formed by floating on mercury.

Tamai and Tamaka[12] investigated the advancing contact angle of acrylate films made on different metal substrates (Cd, Ni, Al, Fe, Au) and compared the results with a mechanical test (breaking weight). They found that the contact angle of the air-side of the film was the same for all the films investigated. The advancing contact angle and the breaking resistance of the substrate-side of the film varied markedly according to the metal employed. The biggest difference between air- and metal-sides was for Cd and decreased in the order: Cd, Ni, Al, Fe, Au. The authors came to the conclusion that these differences meant that the nature of molecular structure of the film on the air-side differs markedly from that on the metal-side.

Thus, in the above cases, there are indications that the substrate can induce orientation of the chain molecules during film growth.

The phenomenon of orientation induced by substrate may take place for every inhomogeneous film formed on a substrate. A polar substrate will attract polar parts of the high molecular weight chains, while the non-polar parts may concentrate at the film/air interface. Low molecular weight materials of higher polarity may gather at the metal/film interface and an inhomogeneity may develop in the film structure. Therefore, different film structures may result for the same polymer film formed on substrates differing in the polarity of their surfaces.

Inhomogeneity in film structure might be demonstrated by differences in water vapour permeability, according to the type of substrate employed and the side of the film exposed. When the lower side of the film is facing the water vapour, the permeability values might be expected to be higher than the values obtained when the air-faced side of the film is directed to the water.

The same film thickness will be permeated in both settings, but the wettability of the lower surface of the film may be much higher than that of the upper surface; consequently, changes which depend on wetting and weight concentration of water, such as swelling and diffusion, could be promoted.

One of the purposes of this research programme was to confirm experimentally the theories discussed above.

Experimental

In the work here reported, different factors affecting water vapour permeability were studied. Special attention was directed to solvent and substrate influence.

Three polymers were tested: nitrocellulose, chlorinated rubber and alkyd. (Formulae given in the Appendix.) The choice was governed by the different polar characters, the type of drying and curing mechanism. The solvents used were typical commercial materials.

The solutions were cast on polyethylene, glass, tin foil or photographic paper, using the ICI Spinner.

The films were dried at room temperature: nitrocellulose and chlorinated rubber films for one to two days and alkyd for a week, at least. Then the films were stripped mechanically or by amalgamation of the tin; the photographic paper was soaked in distilled water in order to free the polymer film. The film thickness was measured with a micrometer.

Water vapour permeability was followed using aluminium Payne cups of 10cm^2 area and 1.5cm height. Each cup contained 10ml distilled water and was sealed by the test film. The film itself was tightly secured between silicone greased flange and cup lid by screws. No water vapour leakage through the flange connection was detected when checked in a blank test secured with a tin foil.

The tests were carried in a closed brass cabinet controlled by a precision hygrometer. The relative humidity of *ca* 20 per cent in this cabinet was achieved by silica gel dehydrating agent.

The cabinet was contained in a thermostatic bath at 38°C ± 1.1°C. (The temperature is above any possible T_g point of the paint films; the permeability at this temperature is about three times the permeability at 23°C).

The cups were weighed every 24 hours and the weight loss was recorded. The data are plotted in graphs, as this way of representation was felt to be more illustrative and comparative.

Results

Nitrocellulose lacquers

Films of 5-second nitrocellulose (NC) were cast from ethyl acetate solution on tin foil, polyethylene, photographic paper and glass. The data are represented graphically in Fig. 1. The water vapour permeability (wvp) values of the films were found to be in the following order: highest for films made on glass, then on tin foil, photographic paper and the lowest on polyethylene substrate.

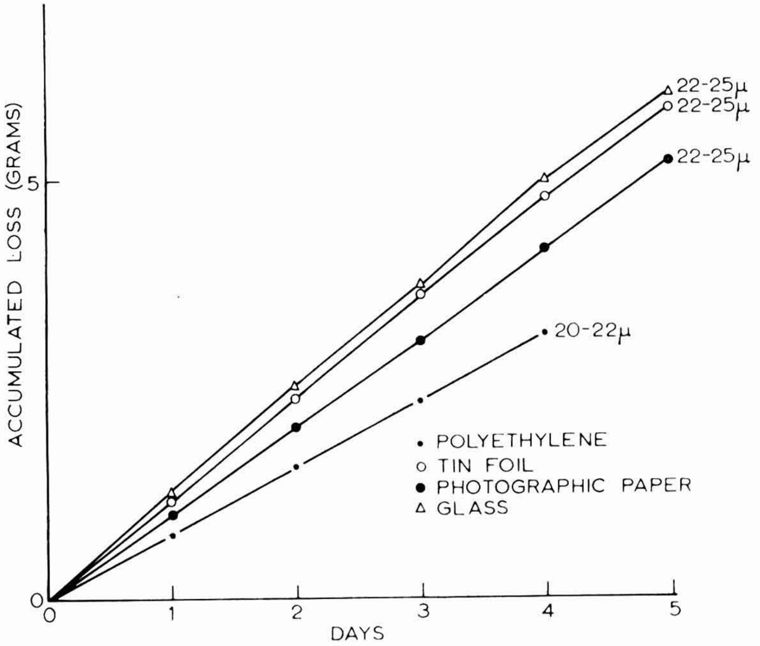


Fig. 1. The substrate influence on water vapour permeability of nitrocellulose films

In order to examine the solvent influence on the film permeability, solutions were prepared in ethyl acetate, in methyl ethyl ketone and in ether:ethanol mixture (Fig. 2). The highest wvp was obtained for films cast from methyl ethyl ketone (MEK), then from ethyl acetate, while the lowest was from ether: ethanol solution.

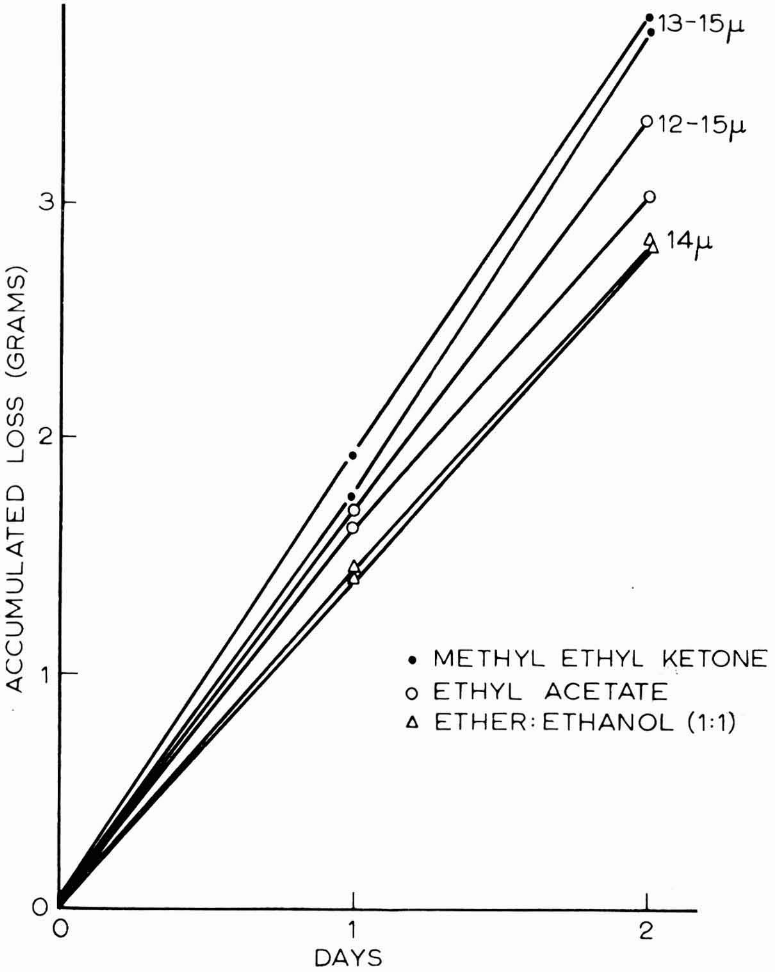


Fig. 2. The influence of the solvent on water vapour permeability of nitrocellulose films

The influence of variations of solvents in solvent mixtures (solvent + diluent) on the wvp was examined with the following common mixtures: ethanol: toluene:ethyl acetate *versus* ethanol:toluene:isobutyl acetate (Fig. 3).

The results showed higher wvp values for the films cast from ethyl acetate solution than for those applied from isobutyl acetate solution.

Chlorinated rubber lacquers

The substrates used for the casting of chlorinated rubber (CR) films were polyethylene and tin foil. Glass was rejected as a substrate since the stripping damaged the film. The photographic paper was rejected as a substrate since treatment with distilled water (required for separation of the film from the surface) was suspected to influence the results. The data obtained (see Fig. 4) showed a lower wvp for tin foil cast films than for polyethylene cast.

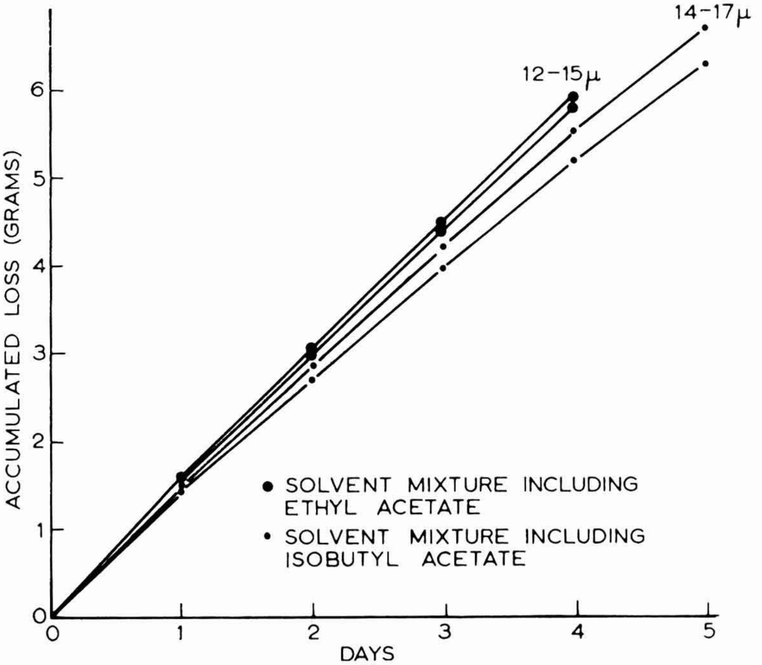


Fig. 3. The influence of solvent on water vapour permeability of films made from solvent mixtures of nitrocellulose

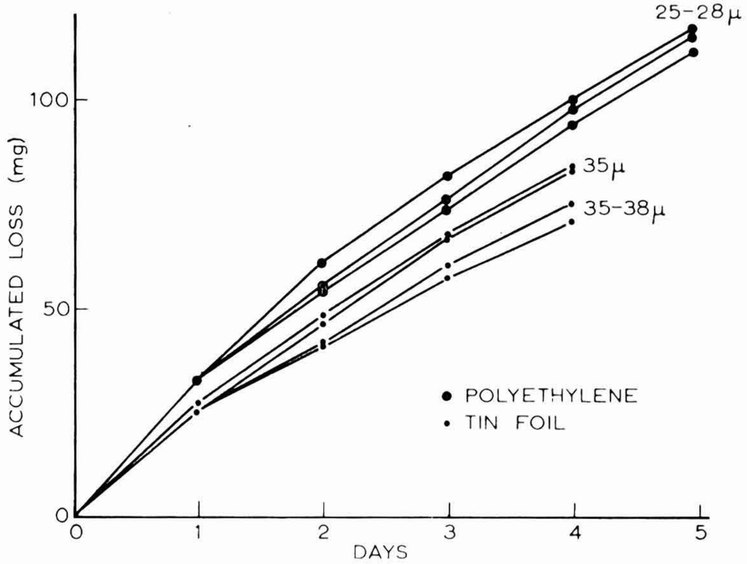


Fig. 4. The influence of substrate on water vapour permeability of chlorinated rubber films (Chlorinated rubber: plasticiser: solvent 5:1:10)

The solvents used in chlorinated rubber solutions were methyl isobutyl ketone (MIBK), xylene and trichloroethylene.

As the plasticiser is also believed to have influence on the wvp, according to type and proportion to binder, two different percentages of plasticiser were tried.

For films cast from solutions of lacquer of a binder:plasticiser:solvent proportion of 5:1:10 (Fig. 5) the order of wvp was: highest for the films from methyl isobutyl ketone solution, then xylene and lowest from trichloroethylene.

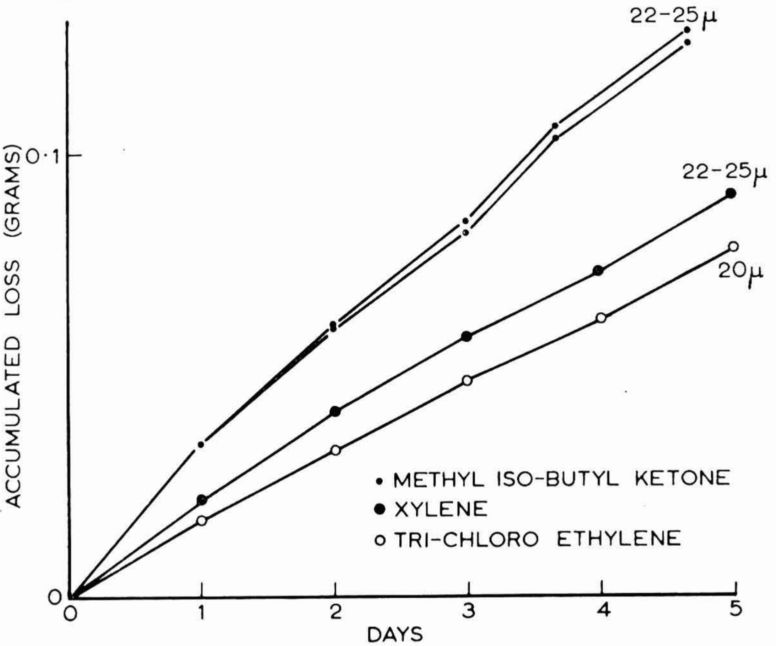


Fig. 5. The influence of solvent on water vapour permeability of chlorinated rubber films (Chlorinated rubber: plasticiser: solvent 5:1:10)

Films cast from solutions in proportion 2:1:4 (binder:plasticiser:solvent) showed the following sequences of wvp: MIBK solution highest, then trichloroethylene and xylene films, with only small differences between the wvp values (see Fig. 6).

Alkyd resin

Since alkyds possess excellent adhesion properties to most substrates, difficulties were expected when stripping the films. In the event, stripping without damage to the film was possible only from tin foil substrate; thus no comparison was available for other substrates.

The solvents used for alkyd solutions were "Octaro" (high boiling solvent naphtha), butyl acetate and methyl isobutyl ketone (Fig. 8). The wvp values obtained descend in this order, the highest being for films cast from "Octaro" solution.

Discussion

The influence of the solvent

In order to understand the sequence of wvp values obtained for films cast from different solvent mixtures, several factors should be taken into account:

physical properties of the solvent such as boiling range, evaporation rate, molecular weight and chemical structure, affinity to resin, drying rate of the film and, specifically, solvent retention.

The kinetics of drying may play an important role in the organisation of the film structure. For instance, ethyl cellulose films cast from toluene solution[6] have a higher elongation and tensile strength than films from ethanol solution. Thus, the structure formed from ethanol must be more dense. Kinetics of film formation showed that three-dimensional growth begins in films cast from ethanol solution at lower polymer concentration. At this concentration, the polymer molecules are still able to move and to organise into a dense film structure.

In toluene solution, the three-dimensional growth is delayed until evaporation to a higher polymer concentration has occurred. At this concentration, orientation is sterically hindered, resulting in a loose dry-film structure which has a higher tensile strength and elongation. This loose structure has also a higher wvp.

For the following discussion the necessary data on solvent properties are tabulated in Table 1. Yet, solids are known to retard solvent evaporation to a certain degree, specific to every solvent-resin combination. Thus, Table 1 should be looked upon only comparatively and to provide a basis for further insight.

Table 1[6a]

	Boiling range °C	Evaporation rate*	Molecular weight
Isobutyl acetate	110-119	174	116
Ethyl acetate	71- 85	615	88.10
Methyl ethyl ketone	79- 81	572	72.10
Xylene	130-145	63	106.10
Methyl isobutyl ketone	114-117	165	100.16
Trichloroethylene	86- 90	620	130.40
Toluene	108.4-112.4	240	92.13
Ether	34- 35	3,300	74.12
Ethanol	74.5- 79.5	340	46
Butyl acetate	118-128	100	116.16
"Octaro"	162-200	16	about 120-130

*against butyl acetate as 100

The specific polar groups of the NC polymer are the ester, ether and hydroxyl groups. On a structural basis, the highest chemical affinity would be expected from ethyl acetate.

The wvp of films from ethyl acetate solution is indeed lower than that from MEK. The reason is probably a better alignment of NC molecules in ethyl acetate solution (the rates of evaporation of the two solvents are almost the same, but a somewhat higher tendency of solvent retention in MEK solution may be noted).

Films of NC from ether:ethanol solvent mixture show the lowest wvp, although each of the components is not by itself a solvent for the polymer. Wright[8] attributes the high tensile strength found for these films to poor solvent retention. Yet, ether:ethanol mixtures have long been known as good solvents in celluloid production. The mixture was found to contain a molecular ether-ethanol complex[13,14] or a complex of NC with the solvent mixture. The resulting film may have an oriented structure which is responsible for the low wvp and the high tensile strength.

The mixture of ethyl acetate:ethanol:toluene is a better solvent mixture for NC than isobutyl acetate:ethanol:toluene. From the latter solution films of lower wvp are cast. This may be explained by the slower evaporation of isobutyl acetate, enabling orientation of the film before drying.

Chlorinated rubber is soluble in all organic solvents except aliphatics. The wvp of CR films is higher for MIBK solution than for trichloroethylene.

The chemical composition of trichloroethylene is similar to that of chlorinated rubber; therefore the cast film may have the densest structure. MIBK, a voluminous molecule of no chemical similarity, may give an opportunity for the formation of more tangled and less oriented films of chlorinated rubber.

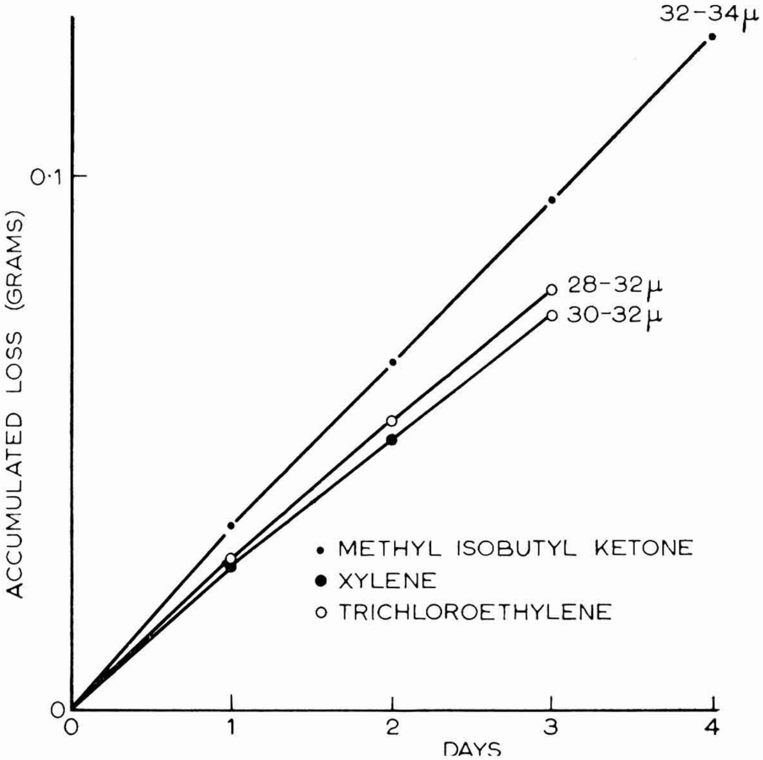


Fig. 6. The influence of solvent on water vapour permeability of chlorinated rubber films (Chlorinated rubber: plasticiser: solvent 2:1:4)

Xylene is very dissimilar to CR and evaporates very slowly; its retention in the cast film is very high; therefore it may allow more development of pores in the dry film than the other solvents. The pores formed in xylene solution films were visible when the film was examined through a microscope, in contrast to the films cast from the other solutions. This would seem to explain the lack of reproducibility of permeability tests encountered sometimes with CR films cast from xylene solutions. Thus, results based on these films were felt to be unreliable and were not drawn on Fig. 7, which sums up the influence of the above solvents on wvp with varying thickness.

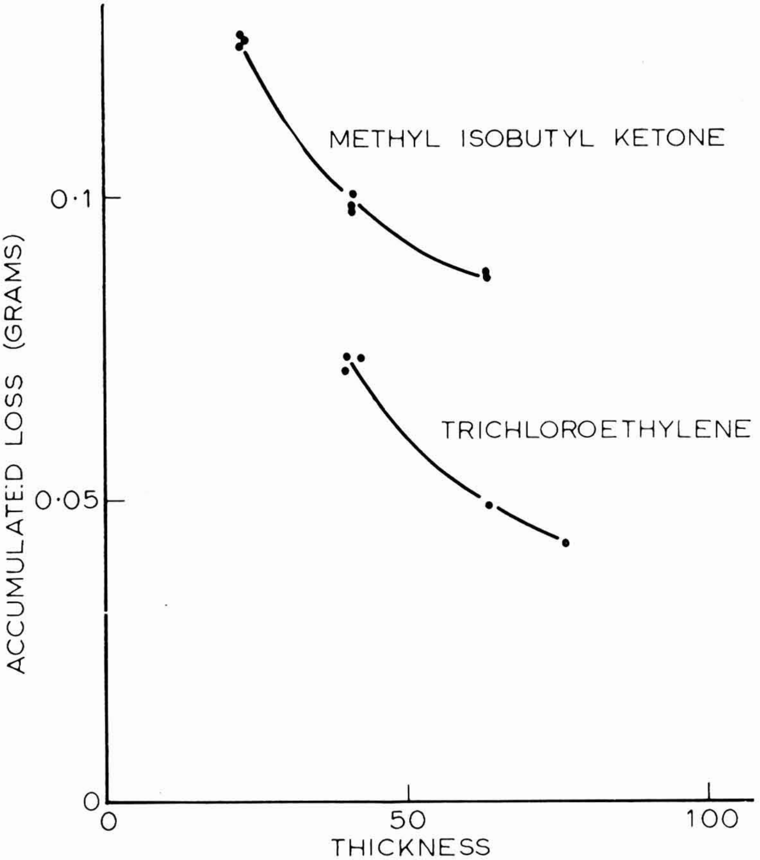


Fig. 7. The influence of thickness on water vapour permeability of chlorinated rubber films (Chlorinated rubber: plasticiser: solvent 5:1:10)

Plasticiser proportion to binder was not found to change the order of the solvent influence; for both ratios, films from MIBK solution had higher wvp than those of trichloroethylene.

Alkyd films are formed by solvent evaporation and oxidation. The evaporation rate has to be slow if it is to influence the process of oxidation. Even for alkyds of the long oil type, used in the experiments above, the first mechanism is more that of evaporation than that of oxidation. Thus the solvent may have some influence on film formation.

The wvp of alkyd films is in decreasing order: "Octaro," butyl acetate, and MIBK. This is also the inverse order of evaporation rate. "Octaro," containing 85 per cent aromatics, is a strong solvent but its structure is totally unlike the structure of the drying alkyd film; hence the high wvp.

MIBK has much similarity to the aldehyde and ketone structures present in oxygenated fatty acid chains; therefore it may very well be that alkyd films cast from this solvent may be better oriented and more dense than from hydrocarbons. Further research may be warranted for this question, which is of great importance.

Butyl acetate with its ester structure has some similarity to the glycerol esters present in the alkyd film, which may explain the medium dense film with medium wvp.

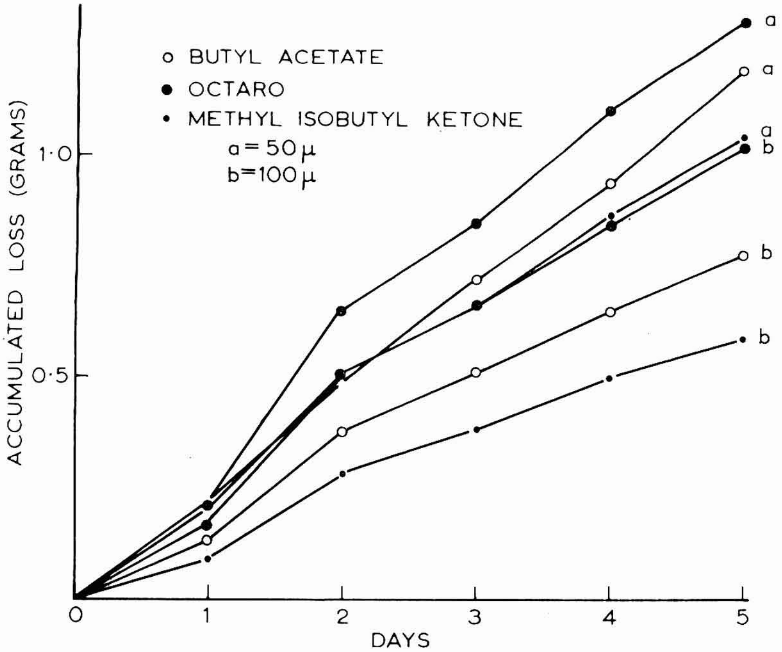


Fig. 8. The influence of solvent on the water vapour permeability of alkyd films (70%)

Influence of substrate

If the substrate surface has any influence on the film formation, it should cause inhomogeneity throughout the film thickness; the lower side of the film, facing the substrate, will contain more polar groups than the upper side facing the atmosphere. The wetting of both surfaces of the film will be different[12]. Thus, if the substrate is expected to exert any influence, there should be some differentiation in the wvp from both sides of the film.

The wvp values of all the films employed in the present study were higher when the substrate side of the film faced the water vapour (see Fig. 9).

The nature of the substrate has a specific influence. The tin foil, like most metals, is covered with a layer of oxide which gives it a polar character. In contrast, polyethylene has no polar groups in its structure; thus its surface has a non-polar character.

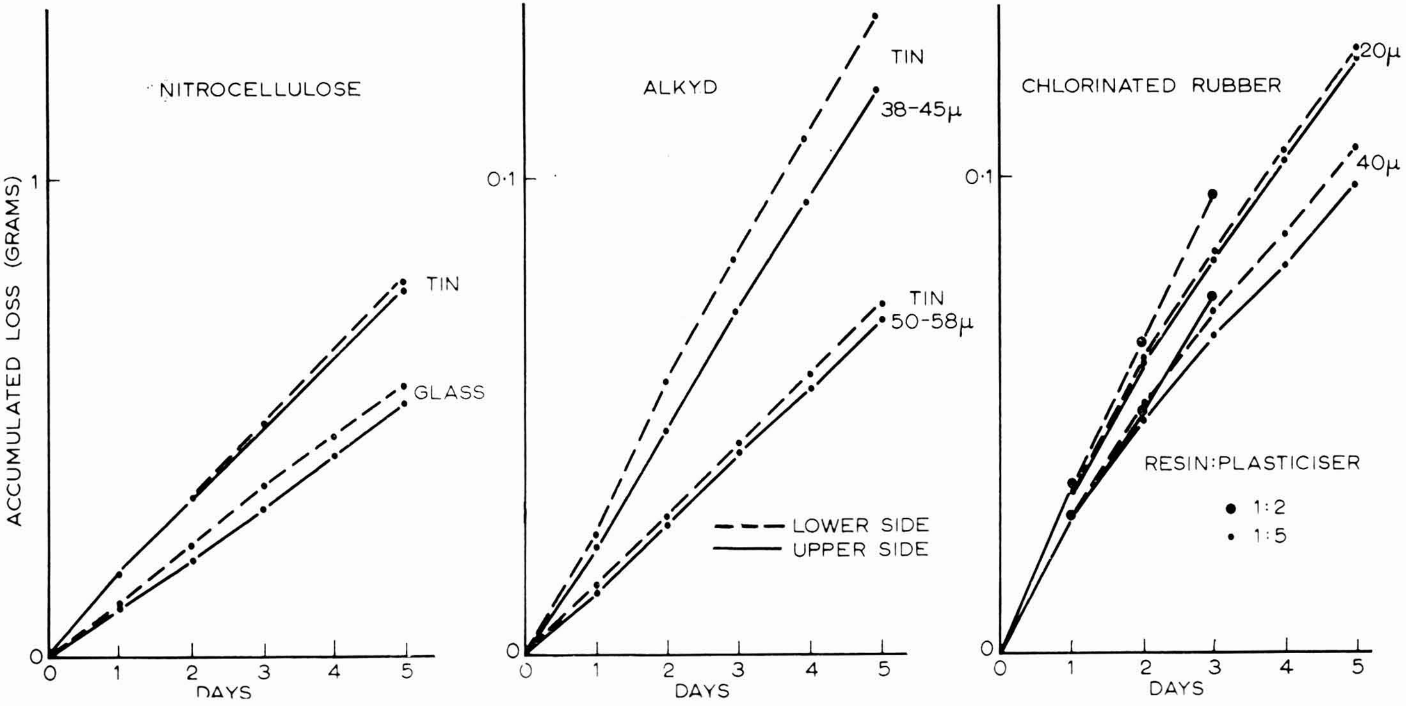
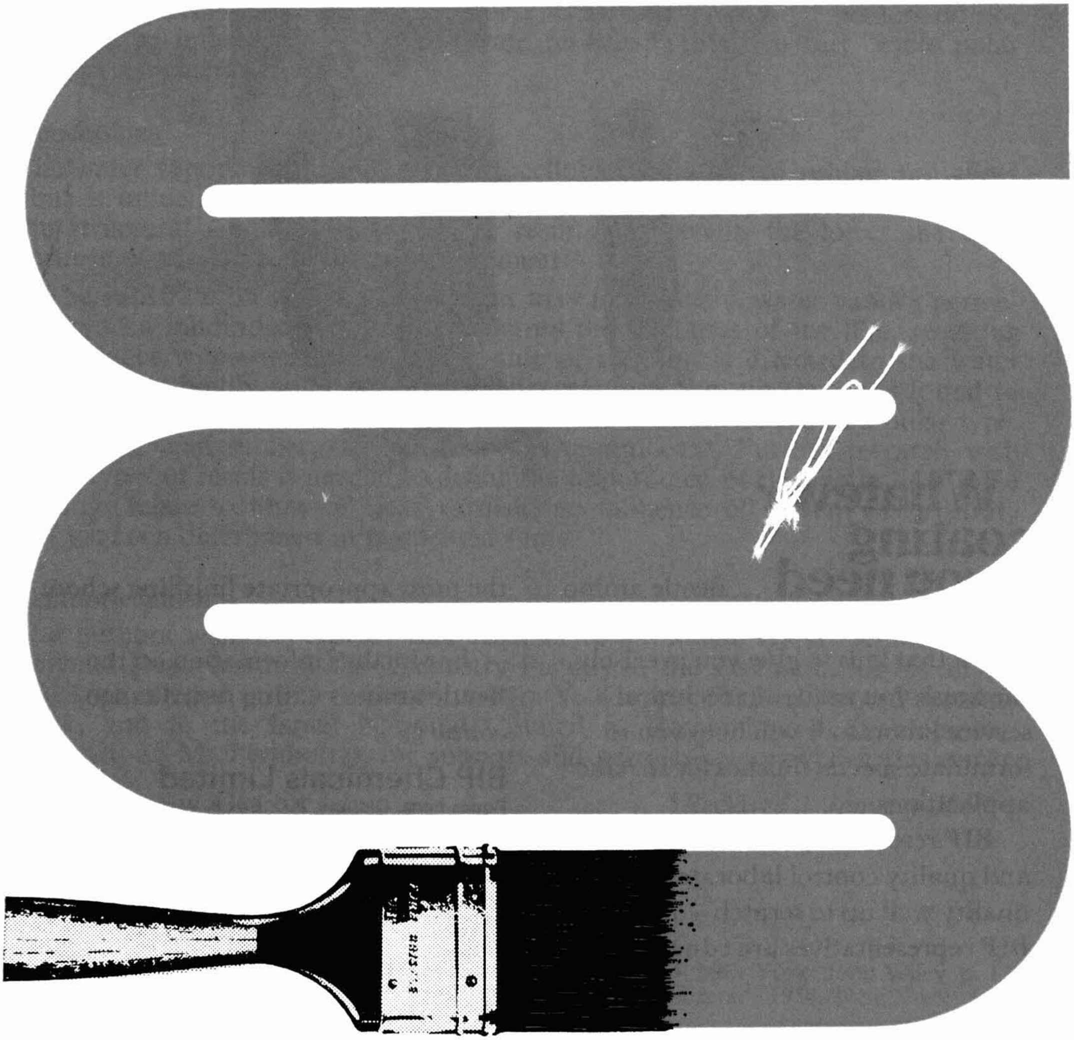
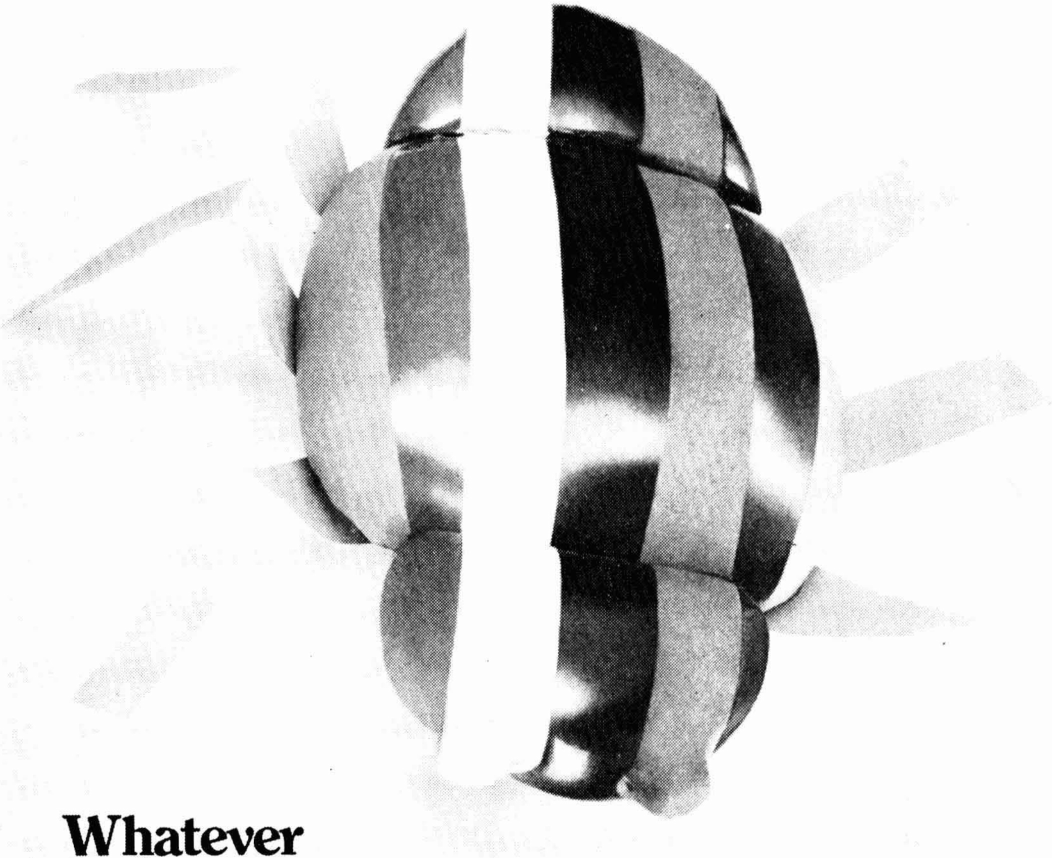


Fig. 9. The influence of the side of the film (upper or lower side) which is directed to the water vapour on the film permeability





Films cast on polar substrates may have a higher degree of inhomogeneity than those applied on non-polar substrates. Therefore, a higher wvp through the lower film surface should be found for films cast on polar substrates (tin foil) than for those cast on non-polar substrates (polyethylene). The differences would be expected to be more pronounced when the binder itself is polar, as it will then be oriented more by the polar substrate. Polar polymers have also a higher order of magnitude of wvp than the non-polar binders, so that differences should be more significant.

Thus, NC films cast on tin foil have higher wvp values than films cast on polyethylene. The difference in permeation is more than 2g water (from a total of 10g) in five days.

Chlorinated rubber films have a somewhat higher wvp when cast on polyethylene than on tin foil: the difference is 30mg in five days. This difference is not expected to be significant: as chlorinated rubber is a binder of a known low wvp, it could arise from error scattering and thickness variations. Non-polar binders do not seem to be influenced by the substrate on which they are cast, while polar binders are clearly affected.

Conclusions

The water vapour permeability of nitrocellulose, chlorinated rubber and alkyd films is influenced by the type of solvent used in their formation. The closer the structural similarity between the resin and solvent, the lower the wvp, because of favourable molecular alignment.

The substrate on which a film is cast may influence its water vapour permeability. An inhomogeneity develops across the thickness of the film, resulting in a higher wvp when the substrate-side of the film is directed to the water vapour. For highly polar resins, like nitrocellulose, the substrate was found to influence the wvp of the film which was cast on it, while for the non-polar type, like chlorinated rubber, the influence was insignificant. Further research with other types of resins is needed to define the importance of this factor. All these findings relate to films of clear varnish; no influence of solvent or substrate has yet been determined in pigmented films.

Acknowledgments

The authors wish to express their thanks to Professor D. H. Kohn of the Polymer Department of the Chemistry Faculty at the Technion, for his advice and keen interest in this research, to Mrs Y. Klopper for her devoted accurate work, and to the Israel National Council of Research and Development, especially to Mr Perlmutter, for support and permission to publish this paper.

[*Received 1 January 1969*

References

1. Leibovits, A., *Modern Plastics*, 1966, **43** (7), 139.
2. *TAPPI*, Monograph 23, 1962.
3. Morgan, P. W., *Ind. Eng. Chem.*, 1953, **45,** 2296.
4. Moll, W. L. H., *Kolloid Zeit*, 1964, **195,** 43.
5. Payne, H. F., "Organic Coating Technology," Vol. I, 1954, New York: John Wiley, p. 17.
6. Doolitle, A. K., "The Technology of Solvents and Plasticizers," 1954, New York: John Wiley.

6a. *Ibid*, Table 11.1, p. 380.
7. Kunze, K. S., *Farbe und Lack*, 1956, **62,** 372.
8. Wright, P. D., *JOCCA*, 1956, **39,** 144.
9. Kriston, P., and Dimitrov, M., *Plaste u. Kaut*, 1964, **11,** 77.
10. Kriston, P., and Dimitrov, M., *Plaste u. Kaut*, 1965, **12,** 74.
11. Kriston, P., and Dimitrov, M., *J. Polymer Sci.*, 1967, C, (16), 2077.
12. Tamai, Y., et al., *J. Appl. Polymer Sci.*, 1967, **11,** 297.
13. Baker, F., *J. Chem. Soc. Transactions*, 1913, **103.2**, 1653.
14. Durrans, T. H., "Solvents", 7th ed., 1957, London: Chapman and Hall Ltd.
15. *Bureau, Corrosion, Traitements etc.*, 1968, **16** (5), 235.

Appendix

a. Nitrocellulose lacquer:

Nitrocellulose (5 sec) (Hercules)	12.2	g
Ethyl alcohol	22.7	„
Toluene	49.0	„
Ethyl acetate	18.0	„

b. Chlorinated rubber lacquer:

Chlorinated rubber (Allopren 20)	50	g
Chlorinated paraffin 43	10	„
"Octaro"	100	„

c. Alkyd resin:

Soya fatty acids	630	g
Phthalic anhydride	230	„
Glycerol	91	„
Pentaerithritol	98	„
Xylene	40	„
Acid No.	8.28mgKOH/g	
Hydroxyl No.	32.9	mgKOH/g

d. Alkyd lacquers:

Alkyd resin	70	g
Xylene	30	„
Anti-skinning agent	0.5	„
Driers	0.5	„

Next month's issue

The Honorary Editor has accepted the following papers for publication and these are expected to appear in the June issue:

"Some factors affecting the brightness and opacity of emulsion paint films: —IThe Stereoscan electron microscope," *by J. Fairless.*

"Management by objectives in research and development," *by G. S. Sanders.*

"Long term adhesion studies on multicoat systems exposed to natural weathering," *by P. Walker.*

"Polarographic study of the effect of additives on the aggregation of dyes," *by Wahid U. Malik and S. M. Saleem.*

Review

TESTING OF POLYMERS. VOL. 3.

By J. V. SCHMITZ and W. E. BROWN (Editors). New York: Interscience Publishers: 1967. Pp. xi+379. Price 185s.

Last year we expressed our appreciation of the first two volumes of this series, and it is a pleasure to record that their high standard is maintained in Volume 3.

The accent in this volume is on surface properties and wear testing, and our readers are likely to be most interested in Boor's introduction to surface property testing and the chapters on indentation hardness testing and wear testing by Livingston and Gavan respectively. A contribution of general interest is that of Roth and Mahmoodi on special tests for temperature effects on physical properties and dimensions. More specialised topics include the evaluation of wear properties of plastics for ships' bearings and the surface properties of plastics for sound recordings.

In a concluding chapter, the editors present selected references on sources of standards and tests for polymers. This could have gone a long way towards meeting our previous request for more cross-referencing of the various national standards but, unhappily, it fails to do so. Whilst ASTM standards are detailed, British and DIN standards receive the barest mention. It was gratifying to see OCCA's Paint Technology Manual, Part 5, listed among the useful source books but this was small compensation for the omission of JOCCA (and several other important British and European journals) from the list of periodicals.

The brief appendix on the conversion of English units to metric units could profitably be expanded in a future volume, when it is to be hoped that the SI system will be fully detailed.

Notwithstanding its continued preoccupation with Transatlantic procedures and test instruments, this series can still be warmly recommended. The careful treatment of underlying theory is alone sufficient to warrant the serious study of these volumes by all concerned with the testing of polymeric materials.

A. R. H. TAWN

STUDENT CONTRIBUTION

The analysis of the leachate of anti-fouling paints using polarographic techniques*

By I. R. McCallum

P. W. Hall Ltd., Kirkintilloch, Glasgow

Summary

The leachates of panels of anti-fouling paints, immediately after immersion in sea water 24 hours after application, and after 75 days immersion were analysed using the single sweep cathode ray polarograph.

After standardising the procedure, very accurate results were obtained, the concentration of lead and tin being determined at levels as low as 0.005μg.ml^{-1} in the presence of copper. These results were reproducible and, on further examination of the results listed at the end of the paper, one can assess the capabilities of this instrument.

Key words

Types of coating
anti-fouling coating

Binders etc
oleoresin

Prime pigments
copper oxide

Methods primarily associated with analysis or testing
polarography

L'analyse, au moyens des techniques polarographiques, des extraits a l'eau de mer des peintures anti-fouling

Résumé

On a appliqué des peintures anti-fouling aux éprouvettes, et après 24 heures les immergées dans l'eau de mer pour 75 jours. Puis les extraits ont été immédiatement analysés au moyens d'un tube cathodique à monobalayage.

Après la normalisation du procédé, on a obtenu des résultats très exacts et reproductibles. On a dosé les concentrations de plomb et d'étain aux niveaux aussi faibles que 0.005 μgrammes par ml. en présence de cuivre. On peut apprécier les possibilités de cet instrument par une considération des résultats mentionnés à la fin de l'exposé.

Die Analyse der Auslaugestoffe aus Antifoulings unter einsatz Polarographischer Techniken

Zusammenfassung

Die Auslaugestoffe aus mit Antifoulings gestrichenen Tafeln wurden unmittelbar nach Immersion in Seewasser, 24 Stunden nach Anstrich und nach 75 Tage dauernder Immersion, mittels des "single sweep" Kathodenstrahlen—Polarographs analysiert.

---

*Adapted from LRIC thesis.

Sehr genaue Resultate wurden erhalten, nachdem ein Standard für die Analysenmethode festgelegt worden war. Selbst so niedrige Konzentrationen von Blei und Zinn als 0.005 μg ml^{-1} wurden bei Gegenwart von Kupfer bestimmt. Diese Ergebnisse waren reproduzierbar. Bei weiterer Prüfung der am Ende der Abhandlung aufgeführten Resultate können die Anwendungsmöglichkeiten dieses Instrumentes beurteilt werden.

Анализ выщелачиваемого продукта необрастающих красок, применяя полярографическую технику

Резюме

Анализировались выщелачиваемые продукты на панелях необрастающих красок тотчас же после их погружения в морскую воду 24 часа после применения, и после 75-ти дней погружения, применяя однозразвертный катодно-лучевой полярограф.

После стандартизации процесса, были получены весьма точные результаты. Концентрация свинца и олова были определены на низких уровнях до 0.005 мкг. мл$^{-1}$, в присутствии меди. Эти микромасштабные результаты воспроизводимы и после дальнейшего изучения данных приведенных в конце статьи, можно сделать оценку способности этого прибора.

Introduction

The fouling of the underwater surfaces of ships by the growth of marine organisms produces increased frictional resistance, raises power requirements to maintain speed, increases fuel consumption and accelerates corrosion. Paints being used to overcome this problem function by releasing poison at a carefully determined rate. This rate of release of poison from the paint film is known as the leaching rate and the successful function of the antifouling composition depends entirely on the effective control of the rate at which the toxicant leaves the paint film. The leaching rate is expressed in micrograms per square cm of paint film per 24 hours, and from extensive research it has been found that the most economic rate for cuprous oxide, one of the most widely used poison pigments, is 10 micrograms of copper per square cm per day.

The table[1] below shows the leaching rate of copper to prevent the attachment of common types of fouling growth.

Table 1

Organism	leaching rate μg.cm.$^{-2}$ day^{-1}
Weed	2–10
Acorn barnacle ..	8–10
Goose barnacle ..	10
Tube worms	2–10
Mussels	2
Hydroids	4–10
Sea Squirts	2

The experiments, detailed below, were carried out to establish a suitable technique for leaching rate determinations using a cathode ray polarograph.

Details of anti-fouling paints involved in tests

There are two types of anti-fouling compositions which have different leaching rate mechanisms. These are the soluble matrix type and the contact leaching type.

The leaching rate of the soluble matrix type is controlled by the gradual dissolution of the medium or binder, so releasing the pigment toxicant which is being continually exposed at the surface. The binder is therefore the factor controlling leaching rate and it is usually composed of a mixture of natural rosin and its derivatives.

The matrix or binder in the contact leaching type is relatively insoluble but the paint contains a very large proportion of cuprous oxide (toxicant) pigment. The principle behind this type of formulation is that with the high pigment loading the pigment particles are in contact with each other, and so when a particle of cuprous oxide leaves the surface of the paint film owing to dissolution, then another particle is immediately exposed. This is a slightly more sophisticated type of anti-fouling paint and has a longer and generally more effective life than the former type but, due to the larger percentage of cuprous oxide in this paint, it is considerably more expensive.

As mentioned, the most widely used toxicant in these paints is cuprous oxide. Recently, however, investigations and practical tests have shown that replacement of some of the pigment poison by organo-tin or organo-lead poisons enhances the anti-fouling properties.

In the present work, paints were prepared according to two standard formulations of the United States Navy. Details are given in Appendix A.

The six paints were:

1. soluble matrix type—Formula 105(Mil.P.19451).
2. same as (1) but 30 per cent of pigment volume of cuprous oxide replaced by equivalent volume of tributyltin oxide.
3. same as (1) but 30 per cent of pigment volume of cuprous oxide replaced by equivalent volume of triphenyllead acetate.
4. contact leaching type Formula 121(Mil.P.15931A).
5. same as (4) but 30 per cent of pigment volume of cuprous oxide replaced by equivalent volume of tributyltin oxide.
6. same as (4) but 30 per cent of pigment volume of cuprous oxide replaced by equivalent volume of triphenyllead acetate.

With the above six paints, the leaching rates of the two fundamental types may be determined and the relative leaching rates of organo-tin and organo-lead complexes may be compared with the leaching rate of the copper present.

Details of the single sweep cathode-ray polarograph

Before the single sweep cathode-ray polarograph is discussed in any detail, the general principles of polarography will be considered.

The cell used must possess a large, non-polarisable electrode, usually a pool of mercury, and a very small polarisable electrode, i.e. the dropping mercury electrode, shown in Fig. 1.

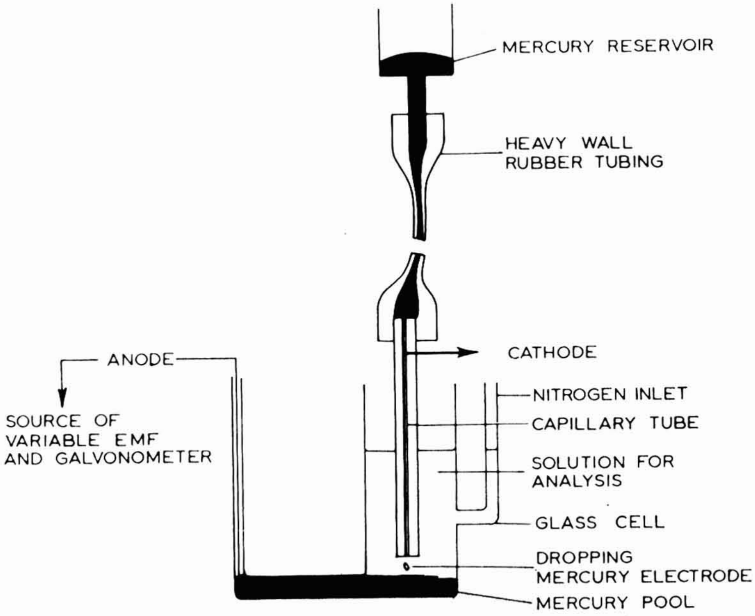


Fig. 1. Dropping mercury electrode

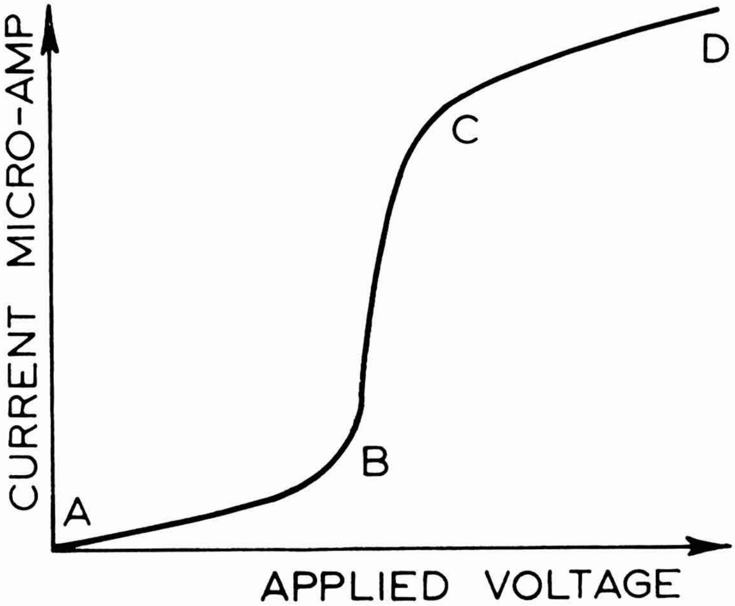


Fig. 2. Plot of current vs voltage for polarograph cell

On applying an external EMF to an oxygen-free solution of copper ions, all the positively charged ions will be attracted to the cathode by two forces:

(a) migration due to electrical attraction of opposite charges

(b) diffusion as a concentration gradient is produced by the loss of positive ions from the solution due to the reaction at the cathode.

The resulting current passing through the cell is assumed due to two factors. A typical current/voltage plot is shown in Fig. 2.

As the applied potential is increased, very little current flows until point B is reached and at this point the potential is equal to the deposition potential of copper. Then immediately the current increases as the copper ions are discharged from the solution. As voltage is further increased (CD) the rate of increase in current falls to a limiting value.

On the polarographic wave BC, the rate of supply of positive ions exceeds the rate of deposition; the rate of supply being controlled by the two processes, cation diffusion and migration. Current due to migration may be eliminated completely by adding an indifferent or supporting electrolyte at about 100 times the concentration of copper ions. This conducts the current leaving the electroactive copper to reach the electrode only by diffusion.

Ilkovic (1934) examined the various factors governing diffusion currents and deduced the following equation.

$I_d = 706\, n\, m^{\frac{2}{3}}\, D^{\frac{1}{2}}\, t^{\frac{1}{6}}\, C$ micro amps.

I_d	diffusion current
n	number of electrons involved
D	diffusion coefficient of the reducible substance in cm^2 sec^{-1}
m	weight of mercury flowing through capillary tube in g. sec^{-1}
t	time in seconds
C	concentration m.moles l^{-1}

Constant temperature is maintained in the cell so that D remains constant; t may vary slightly due to interfacial tension at the mercury/solution interface but the effect on I_d is negligible

Hence $I_d = K.C$ where K is a constant

One important qualitative factor is the half-wave potential, which is characteristic of the species being reduced. It is the potential at the point on the polarographic wave where the current is equal to one half the diffusion current. It is independent of electrode characteristics.

When the voltage sweep is slow, a number of disadvantages occur owing to current oscillations as the mercury drop grows and falls, with the result that the curve is not smooth as expected. This is overcome by using the single sweep cathode-ray polarograph[2]. The main difference is that one sweep of potential covers the life of one drop of mercury as it grows at the bottom of the capillary tube. With a drop time of 7 seconds, the mercury is allowed to grow for 5 seconds and the potential is swept in the last 2 seconds of its life. The cathode-ray tube follows the rapid current change easily and use of a long persistence tube enables the operator to note the position and height of the sweep carefully. In this way, oscillations are eliminated and enhanced resolution occurs between different species present in the same solution whose half-wave potentials differ by only 40 millivolts. This results in a very sensitive detector capable of quantitative analysis of copper in solution at about 10^{-6} molar concentration.

Because of the fast potential sweep this gives rise to a maximum peak whose height is proportional to the concentration, as shown in Fig. 3.

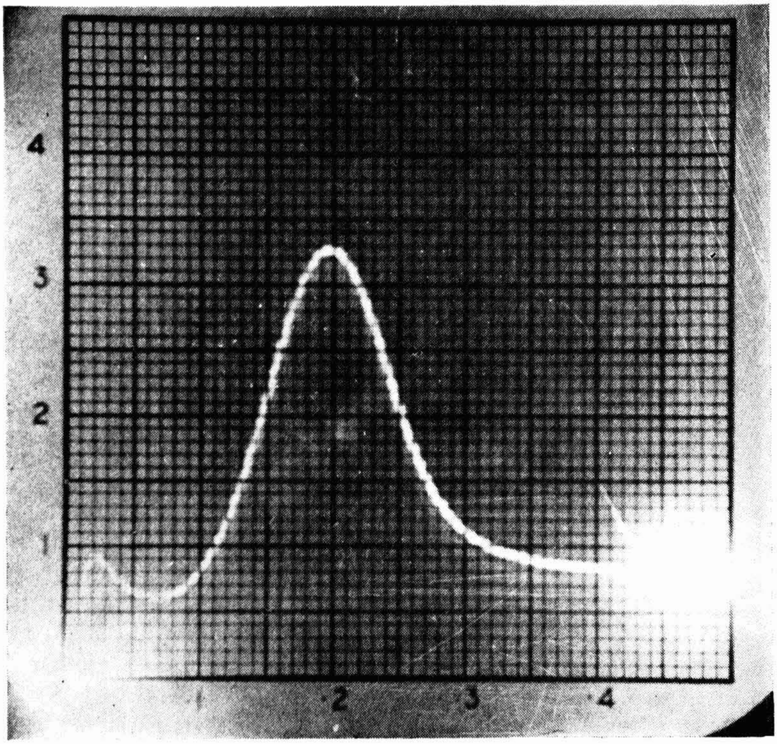


Fig. 3(a). Photograph of polarogram

Experimental details

The paints were prepared as described in Appendix A and panels were prepared in duplicate by applying the paints using a cube applicator at a wet film thickness of 3 thousandths of an inch to glass strips. The glass slides 12in long and 1in wide were lightly abraded by very fine sand blasting prior to application, to give a better key for the paint films.

One set of six slides was attached to a frame, as described in Appendix B, and this was immersed 24 hours after application. By arrangement with the Marine Biology Association's Station, Millport, this frame, with the six panels, was totally submerged in sea water for a period of 75 days in the period February to April.

The remaining six slides were then cut into 4cm squares and immersed in a large tank of synthetic sea water made up as described in Appendix C. Into

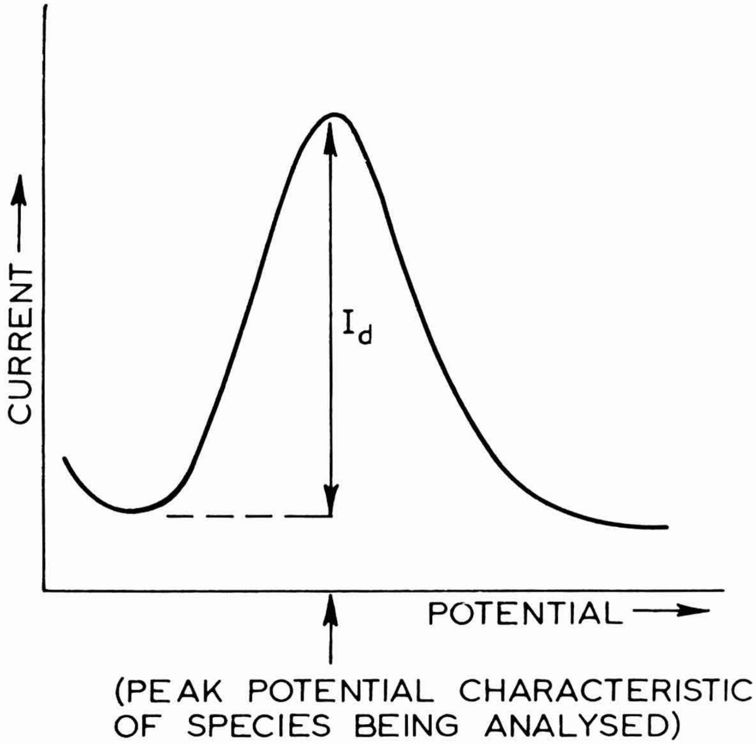


Fig. 3(b). Measurement of *Id*

six 250ml conical flasks was measured 150ml of sea water and into each was placed the 4cm square of glass slide coated with anti-fouling composition. The flasks were then attached to an electrical shaker and agitated for four days. The sea water in the flask was moving about quite briskly, but care was taken that the small panels did not strike the sides of the jar so violently as to damage the paint film. The stoppers had holes in them, allowing access of air to the solution. After four days, the solutions, or leachates, were ready for analysis of appropriate ions.

Before describing the analysis procedure it is worthwhile considering the form of the poisons in solution.

The cuprous oxide, which is sparingly soluble, on initially dissolving in the sea water produces the highly unstable cuprous ions, which are almost all converted to cupric ions and copper

$$Cu_2O \longrightarrow Cu_2Cl_2 \longrightarrow 2Cu^+ + 2Cl^-$$
$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

The copper must be present in the form of a soluble organic complex. It has not yet been confirmed whether the copper or the cupric ions are the lethal ingredients, but it is agreed that anti-fouling paints with cupric oxide as the pigment poison are not as effective as their cuprous oxide counterparts.

The organo-tin and organo-lead complexes are also relatively insoluble, but little appears to be known of the exact behaviour of these organic toxicants in solution.

Analysis procedure

As mentioned earlier, a supporting electrolyte must be present at about 100 times the concentration of the species for analysis. In the present work, sodium chloride was present at a suitable concentration in sea water and so no additives were necessary for the leachate solutions. The solution was placed in the cell with the mercury to form an anodic pool, and was deoxygenated by passing nitrogen through the cell for ten minutes by means of a small side arm in the cell. (Oxygen must be removed as it produces two peaks which generally interfere with cathodic polarographic analysis.)

The equipment was set to give a start potential of —0.05 volts. The peak maximum for copper was found to be around —0.3 volts.

The polarographic analysis, of course, determines only the cupric *ions* in solution. To ascertain the content of Cu resulting from the reaction $2Cu^{+} \longrightarrow Cu^{2+} + Cu$ it was necessary to treat the leachate with perchloric acid to oxidise all available copper to the cupric form. This highly effective oxidation process was carried out as follows.

From the conical flask, 25ml of the leachate was measured into a long necked Kjeldahl flask, and the volume reduced to about 5ml by evaporation. After addition of 2ml of concentrated perchloric acid by pipette, the flask was gently heated until the white fumes of perchloric acid persisted for about five minutes in the flask. The flask was allowed to cool and the mixture washed out and made up to 25ml with deionised water.

The oxidation was carried out in a fume cupboard with precautions against the possibility of explosion.

The resulting solution was then analysed for total copper present, and also for lead and tin in the appropriate solutions.

Calibration graphs were constructed for lead, tin and copper in the sea water/perchloric acid mixtures (23ml sea water, 2ml perchloric acid), and also for copper in sea water (see Figs. 4-7).

The results first obtained on analysis of the various leachate solutions were very inconsistent and rather anomalous, and on investigation it was found that there were two factors interfering with the results.

One source of variation was an unexpectedly large increase in copper content after treatment with perchloric acid, which was found to be due to small pieces of paint film becoming detached from the glass substrate.

The other effect was one of distribution of the cupric ion and copper in the leachate. This was found by decanting 100ml of the leachate, immediately after agitation, into a tall cylinder. This was allowed to stand for seven days and, on visual examination, a very faint colloidal appearance was evident in the bottom section of the cylinder. Samples were then withdrawn from the top, middle and bottom of the cylinder and analysed, with the following results.

Copper concentration in $\mu g.ml^{-1}$	Before acid treatment	After acid treatment
Top sample	2.4	4.2
Middle sample	2.8	5.0
Bottom sample	3.1	10.2

It is interesting to note that the ratio of cupric ions to total copper (before and after acid treatment) is the same in the upper two samples but the bottom sample has a much higher total copper content. This may be due to very small paint film particles, but the evidence of settlement even in the untreated solution indicates a need for a standard sampling procedure. The procedure involved the use of a small air pump which kept the leachate solution in the conical flask under agitation by placing the air outlet at the bottom of the flask. During air agitation, 50ml of the sample solution was extracted using a pipette.

With regard to the small pieces of paint film in the leachate solution after agitation by the shaker, this problem was overcome by applying the paint films to a flat uniform sheet of flexible polyvinyl chloride and then cutting this up into small squares. This flexible pvc offered a better surface for adhesion and did not move about so violently in the conical flask.

Table 1

Paint number	Leachate concentrations of paint films *initially*				Leachate concentrations of paint films after 75 days' exposure			
	Copper A	Copper B	Lead	Tin	Copper A	Copper B	Lead	Tin
1	4.5	9.0	—	—	3.3	6.2	—	—
2	5.0	6.8	—	0.25	4.2	5.7	—	.0375
3	6.0	9.4	0.068	—	4.2	6.2	0.0187	—
4	6.3	6.8	—	—	3.9	6.0	—	—
5	4.5	4.5	—	0.1	2.6	6.2	—	.004
6	3.2	3.2	0.031	—	3.7	6.2	0.014	—

All the above concentrations are in micrograms per ml.

Copper A is the copper present before treatment with perchloric acid.

Copper B is after this treatment and may be called the "total copper."

Before analysis of the sea water/perchloric acid solutions for lead and tin, additions were made to the solutions so that sharper curves were obtained for the extremely small concentrations of these metals. These different supporting electrolytes were originally devised for the estimation of lead and tin in foodstuffs. Details are given in Appendix D.

The complete analysis procedure was repeated using the panels that had been immersed in the Clyde estuary. The frame and panels were transported from Millport to the laboratory in a large polythene sack containing sea water to prevent the paint films from drying out. The painted slides were removed from the frame and cut up into 4cm squares, and each was carefully placed in a conical flask containing 150ml of synthetic sea water and agitated for four days.

A summary of all the concentrations of poisons found in the leachate for each paint initially and after 75 days' exposure in sea water, is given in Table **1**.

Discussion of results

In the four paints which have a combination of organo-lead and copper, organo-tin and copper, the soluble matrix type of binder (paints 2 and 3) allows a faster release of the poisons initially and after 75 days' immersion.

On initial immersion of paint 2 the tin is released at 2.5 times the rate in paint 5. After 75 days' immersion there is a reduction in the leaching rates and then tin is leached from paint 2 at 8.5 times the apparent rate from paint 5.

The actual leaching rates expressed in $\mu g.\ cm^{-2}\ day^{-1}$ for tin after 75 days' exposure are paint 2 0.35
paint 5 0.038

These results show that the tin is leaching from paint 5 at such a low rate that it seems reasonable to assume that the resultant low concentration can hardly be lethal to marine organisms. The manufacturer of this toxicant considers a minimum of 1 $\mu g.\ cm^{-2}\ day^{-1}$ necessary to prevent fouling and has apparently proved this conclusively using tributyltin oxide as the sole poison at tests in waters around Miami, USA. Alternately the leaching rate of tin from paint 2 may be sufficient, together with the high leaching rate of copper, to make it an effective anti-fouling composition.

Both organo-lead/copper anti-fouling paints, 3 and 6, have similar rates after 75 days' immersion but unfortunately no information is readily available concerning the actual concentration of lead lethal to marine organisms.

The relative leaching rates of the copper are all very high and it would appear that the "total" copper leaching from the paint film is not inhibited at this stage by the presence of the organic metal complexes of lead and tin. There is a slight reduction in leaching of copper of paint 2 compared with paints 1 and 3.

The copper A and copper B concentrations vary throughout the chart in relationship to one another suggesting the possible presence of complex copper compounds[3,4] which would vitiate the proposed mechanism. $2Cu^{+} \longrightarrow Cu^{2+} + Cu$

From this equation one would expect the concentration of copper B to be twice that of copper A, but this only occurs in the case of paint 1. It is also rather confusing to note that on initial immersion of paints 4, 5 and 6, nearly all the copper that has leached out appears to be in the cupric state.

Considering the above details, the only relevant determination of copper would seem to be that after treatment with perchloric acid, and it must be assumed that this total copper concentration determines the actual lethal capacity of the solution.

On this proposal, the leaching rate of the copper from the paints is rather high after 75 days exposure, but this leaching rate will fall to a low level which will be maintained throughout the effective life of the paint, i.e. two years.

A typical leaching rate graph[5] is shown in Fig. 8.

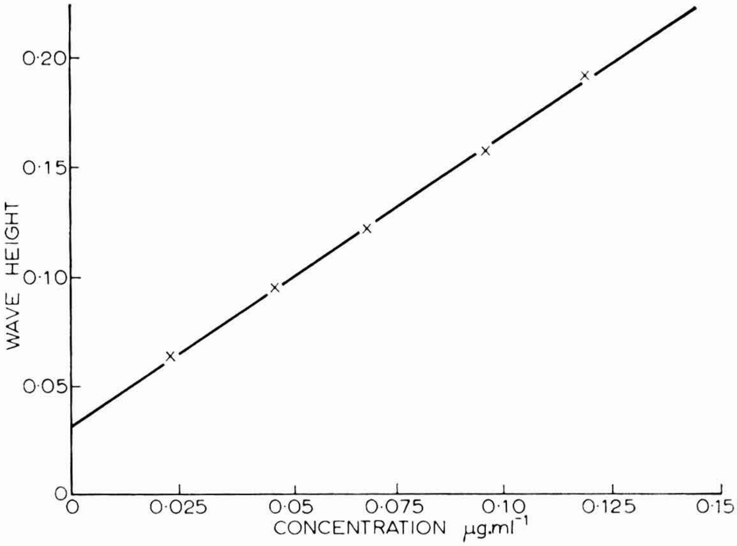


Fig. 4. Calibration graph of lead in sea water/$HClO_4$

Future work

It would be interesting to determine the effect on leaching rates of the organo-lead and organo-tin, increasing their initial concentrations in the paint formulations, and also the effect of temperature, pH and salinity of sea water on general leaching rates. If time were available, then a long term sea water immersion of the above six anti-fouling paints (about 18 months) and comparison of their relative rates with initial results might produce a better picture of the performance of these organo-metal complexes.

Acknowledgments

The author wishes to acknowledge his indebtedness to Mr Hector Munro, Physical Chemistry Department, Paisley College of Technology, for his continual interest and assistance throughout this project.

Appreciation is also extended to Messrs. Craig Hubbuck & Co. Limited and P. W. Hall Limited for the use of their laboratories, and finally to Dr Miller, Mr Latham and staff of the Marine Biology Association's Station at Millport, Bute, for their assistance and use of their exposure facilities.

[Received 25 September 1968
[Revised 20 February 1969

References

1. Paint Technology Manual, Part 4. 1965, London: Chapman and Hall, p. 187.
2. Rooney, R. C., "Principles and applications of cathode ray polarography," Southern Analytical Limited, 1962.
3. Schwarzenbach, C., *Analytical Chemistry* 1960, **32**, 6.
4. Perrin, D. D., *J. Chem. Soc.* 1960, 3189.
5. Partington, A., and Dunn, P. F., *JOCCA*, 1961, **44**, 869.

Appendices

Appendix A

Paint formulations	1.	2.	3.
Copper oxide	589	411	411
Triphenyllead acetate	—	—	77.5
Tributyltin oxide	—	35.5	—
Oleoresinous binder	636	636	636
Zinc stearate	18	18	18
Zinc oxide	161	161	161
Talc	56	56	56
	1460	1317.5	1359.5

Weight per gallon 12.5lb

Paint Formulation 1. —US Navy Formula 105(Mil.P.19451)

Oleoresinous Binder	—WW Rosin	277
	Fish Oil	118
	Xylene	241
		636

Procedure—The rosin was heated to 500°F and allowed to cool to 350°F. The fish oil was added and the resultant mixture heated to 480°F and held at this temperature for one hour. It was then allowed to cool 50°F and thinned with xylene.

Paint formulations	4.	5.	6.
Copper oxide	800	565	565
Triphenyllead acetate	—	—	105
Tributyltin oxide	—	48.5	—
WW rosin	80	80	80
p.v.c./a. copolymer	80	80	80
Tricresyl phosphate	30	30	30
Methyl isobutyl ketone	220	220	220
Xylol	100	100	100
	1310.0	1123.5	1180.0

Paint Formulation 4—US Navy Formula 121(Mil.P.15931A).

Appendix B

The frame for supporting panels for underwater immersion is shown in Fig. 9.

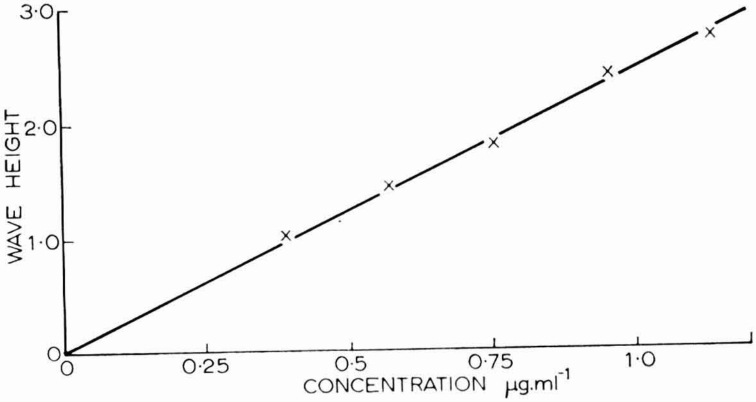


Fig. 5. Calibration graph of tin in sea water/$HClO_4$ mixture

This was painted with two coats of a solvent-free epoxy material followed by a coat of anti-fouling composition (Formulation 1). The glass slides were firmly held in position between wooden blocks and the frame, both being lined with a thin strip of foam rubber.

The frame was then attached to an extension frame eight feet long, as shown in Fig. 10. This was constructed so that the actual panels would be constantly immersed on attaching the large frame to the side of the pier at low tide. As a precaution against mechanical damage due to submerged pieces of wood etc., a piece of wire mesh was finally secured around the small panel as shown in Fig. 11.

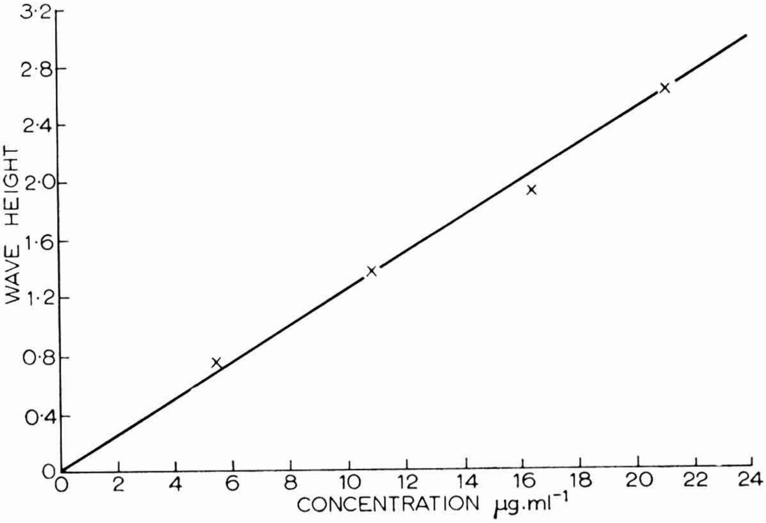


Fig. 6. Calibration graph of copper in sea water/$HClO_4$ mixture

introduction to paint technology

second edition with additional chapter

The sales of this Association publication now exceed 13,000, and because of continuing high sales of the second edition, and the need for a work of reference to be constantly abreast of the latest developments in its field, the Council of the Oil and Colour Chemists' Association has authorised the addition of an eleventh chapter to the ' Introduction to Paint Technology. Entitled ' Recent Developments,' the Chapter incorporates up-to-date information on the latest advances in the technology of the paint and allied industries.

This addition will help the ' Introduction to Paint Technology ' to maintain its position as an invaluable aid to young entrants into the industries and to marketing and other personnel requiring a basic knowledge of the principles and techniques of surface coating production and application.

new chapter

The new chapter is subdivided to three sections

resins and media

Including polyester, epoxy, polyurethane resins and developments in water based paints, vinylics, etc.

application techniques

Including electrodeposition, powder coatings, strip-coating, aerosol spraying.

instrumental testing and control methods

Including colour measurement, viscometers, brushability, hardness, film thickness, weatherometers, and use of computers.

The book contains 204 pages including 11 line diagrams, 8 photographs of common paint defects, and comprehensive index. Copies can be obtained from the Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London E.C.2, price 20s. (post free).

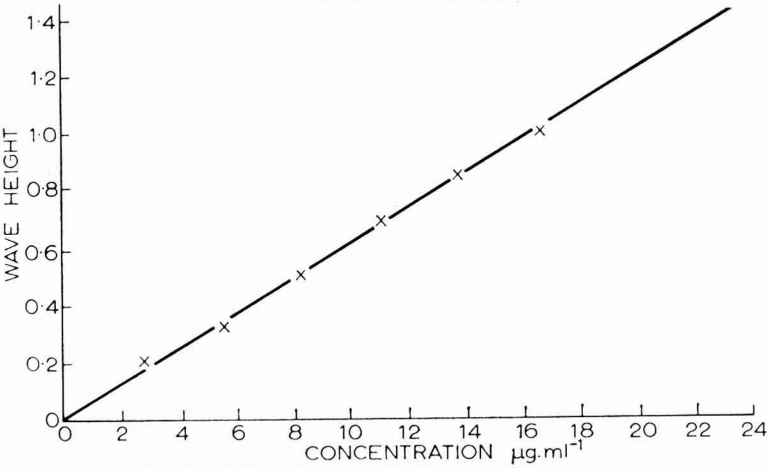


Fig. 7. Calibration graph of copper in sea water

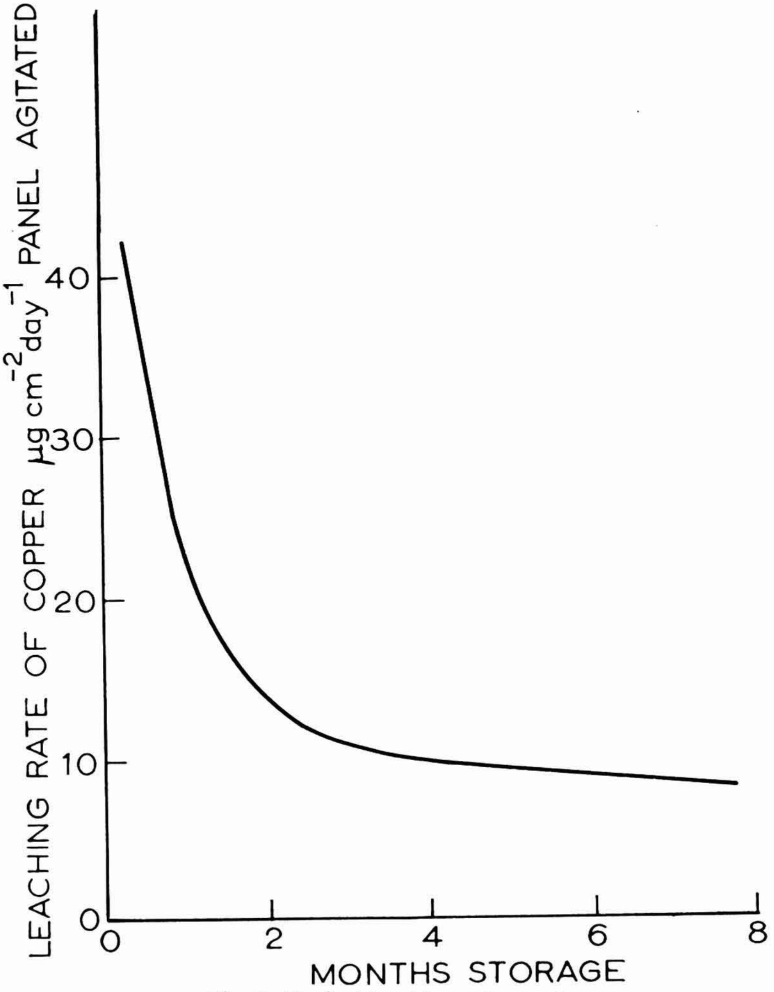


Fig. 8. Typical leaching rate graph

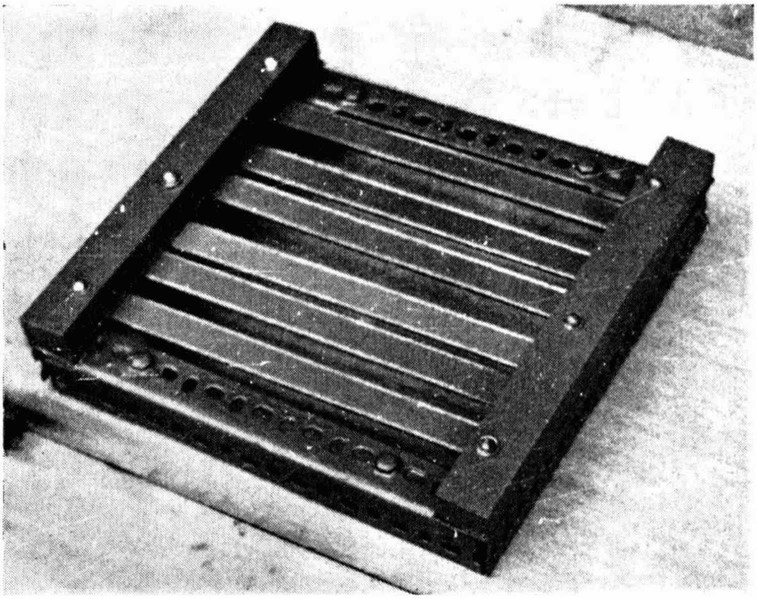


Fig. 9. Supporting frame for underwater panels

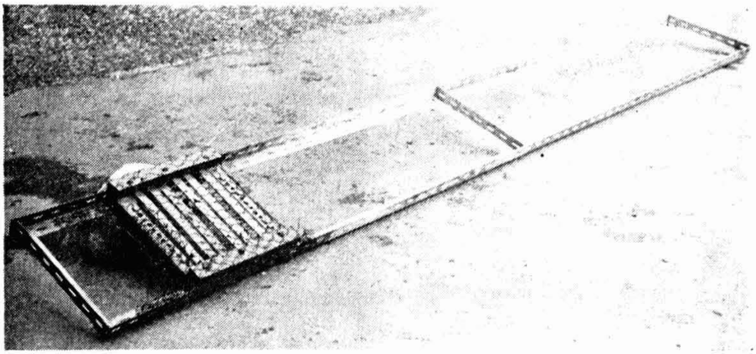


Fig. 10. Extension frame

Appendix C

The synthetic sea water for the laboratory trials was made to an Admiralty Specification and the composition was:

sodium chloride	26.5 g
magnesium chloride	2.4 ,,
magnesium sulphate	3.3 ,,
calcium chloride	1.1 ,,
potassium chloride	0.73 ,,
sodium bicarbonate	0.2 ,,
sodium bromide	0.28 ,,

The above was then made up to one litre with deionised water.

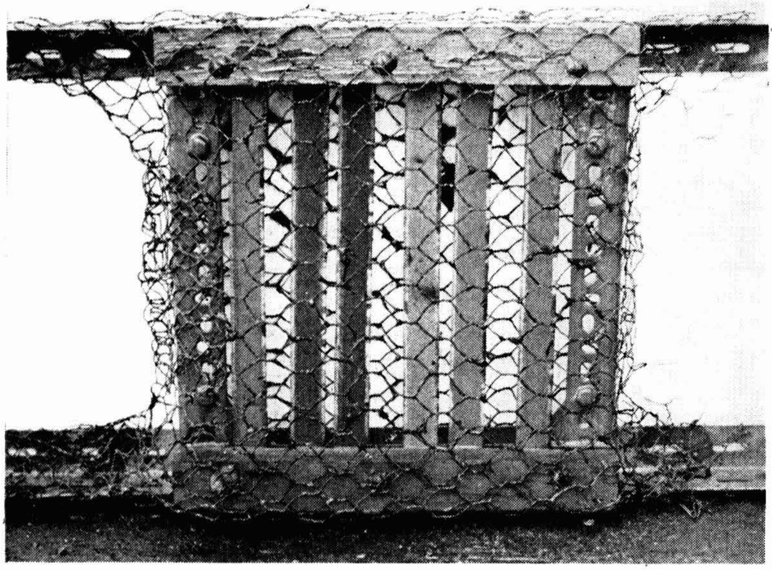


Fig. 11. Method of protecting panels with wire mesh

Appendix D

Analysis of tin

Base electrolyte—100g ammonium bromide
270ml concentrated hydrochloric acid

made up to one litre with deionised water.

Method: a mixture of 2ml of above solution with 2ml of acid oxidised solution was polarographed with start potential —0.20 volts.

Analysis of lead

Base electrolyte—Molar di-potassium hydrogen citrate solution adjusted to pH 1.5 with concentrated sulphuric acid.

Strong sulphuric acid 50% W/V

Strong sodium hydroxide 22% W/V

Method: five ml of acid oxidised solution was transferred into a 10ml flask, 2ml of sodium hydroxide solution and one drop of methyl orange were added, followed by sulphuric acid dropwise until acid. Two ml of base electrolyte was then added and the resultant mixture made up to 10ml with deionised water. This solution was then polarographed with start potential of —0.25 volts.

The theory of functionality, Part III

by A. R. H. Tawn

Cray Valley Products Ltd., St. Mary Cray, Kent

A reaction of functionality 4

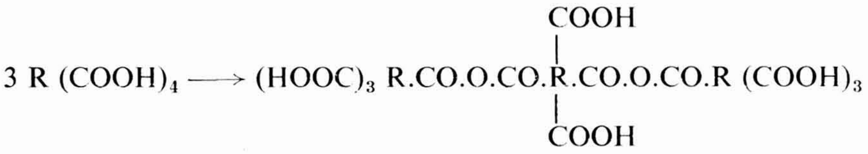
As an example of a tetrafunctional reaction we may consider the intermolecular polyesterification of an equimolar mixture of a tetrahydric alcohol and a tetracarboxylic acid, or the formally simpler formation of a polyanhydride from a tetracarboxylic acid.

Let two molecules of tetracarboxylic acid react to produce a dimeric anhydride ($x = 2$)

$$2\,\mathrm{R\,(COOH)_4} \longrightarrow \mathrm{(HOOC)_3\,R.CO.O.CO.R\,(COOH)_3}$$

Of the $2 \times 4 = 8$ functional groups originally present, 2 have reacted and 6 remain. Hence, when $x = 2$, $p = 2/8$ or 0.25.

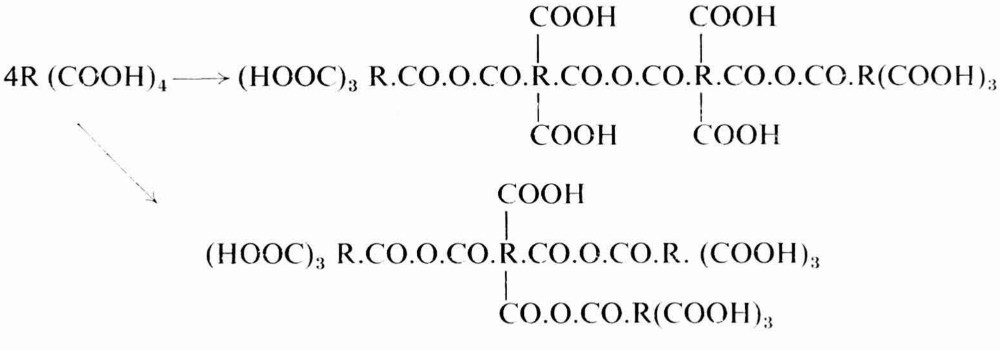
Now let 3 monomer molecules react to form a molecule of trimer ($x = 3$)



$$3\,\mathrm{R\,(COOH)_4} \longrightarrow \mathrm{(HOOC)_3\,R.CO.O.CO.}\underset{\substack{|\\ \mathrm{COOH}}}{\overset{\substack{\mathrm{COOH}\\ |}}{\mathrm{R}}}\mathrm{.CO.O.CO.R\,(COOH)_3}$$

Of the $3 \times 4 = 12$ functional groups originally present, 4 have reacted and 8 remain. Hence $p = 4/12$ or 0.33.

When one considers the formation of tetramer from 4 monomer molecules, it is seen that more than one type of structure can be formed.



$$4\mathrm{R\,(COOH)_4} \longrightarrow \mathrm{(HOOC)_3\,R.CO.O.CO.}\underset{\substack{|\\ \mathrm{COOH}}}{\overset{\substack{\mathrm{COOH}\\ |}}{\mathrm{R}}}\mathrm{.CO.O.CO.}\underset{\substack{|\\ \mathrm{COOH}}}{\overset{\substack{\mathrm{COOH}\\ |}}{\mathrm{R}}}\mathrm{.CO.O.CO.R(COOH)_3}$$

$$\searrow\quad \mathrm{(HOOC)_3\,R.CO.O.CO.}\underset{\substack{|\\ \mathrm{CO.O.CO.R(COOH)_3}}}{\overset{\substack{\mathrm{COOH}\\ |}}{\mathrm{R}}}\mathrm{.CO.O.CO.R.\,(COOH)_3}$$

This does not affect the relationship between p and x, however, for in both cases we have $x = 4$, original functions $= 4 \times 4 = 16$. reacted functions $= 6$ and hence $p = 6/16$ or 0.375.

Similar consideration of the formation of pentamer, hexamer etc. leads to the table:

x	1	2	3	4	5	6	10	100
p	$\frac{0}{1\times4}$	$\frac{2}{2\times4}$	$\frac{4}{3\times4}$	$\frac{6}{4\times4}$	$\frac{8}{5\times4}$	$\frac{10}{6\times4}$	$\frac{18}{10\times4}$	$\frac{198}{100\times4}$

It is not quite as easy to derive by inspection a general relationship between p and x as it was in the case of the bifunctional reaction considered in Part 2, but it can be done with a little thought. The denominator in the expression for p is clearly the total number of functional groups originally present in the monomer, i.e. $4x$, so it only remains to express the numerator also in terms of x. The numerators, set against the values of x, form the series:

x	1	2	3	4	5	6	10	100
Numerator	0	2	4	6	8	10	18	198

and the necessary expression for the numerator may be seen to take the form $2x - 2$.

Hence we may write

$$p = \frac{2x - 2}{4x}$$

and a simple arithmetical check will show that this does indeed represent the relationship between p and x for the 4-functional reaction considered.

Application to other functionalities

If one considers a trifunctional reaction, similar reasoning to that above leads to the expression

$$p = \frac{2x - 2}{3x}$$

It may now be recalled that the bifunctional relationship, deduced in Part 2, took the form

$$p = \frac{x - 1}{x}$$

which can be rewritten

$$p = \frac{2x - 2}{2x}$$

The similarity between this and the tri- and tetrafunctional expressions is obvious.

For reactions of functionalities 2, 3 and 4 the denominators take the values $2x$, $3x$ and $4x$ respectively. It is tempting, therefore, to suppose that a perfectly general expression for reactions of any functionality f may be written by putting the denominator equal to fx thus:

$$p = \frac{2x - 2}{fx}$$

Without more ado, it may be stated that this expression is indeed a general one for intermolecular reactions, a fact that may readily be checked by the reader using the tabulation procedure already outlined. It may also be noted that the expression is more commonly given in the algebraically identical form:

$$p = \frac{2}{f} - \frac{2}{fx}$$

This is the well known equation which was more rigorously deduced by Carothers.

Carothers's deduction of the equation

The somewhat laboured reasoning adopted so far was intended to show that the theory of functionality can be developed in an entirely logical manner without recourse to rigorous mathematical proof. For the more mathematically minded reader, however, the deduction of the equation by Carothers may be reproduced as follows.

Consider the intermolecular reactions of N_o monomer molecules of functionality f. Then the original number of functional groups $= N_o f$.

Let the reaction proceed to a degree p such that the number of molecules present after reaction is N. (Note that N will be smaller than N_o since the original monomer molecules will now be combined into polymer molecules.)

Then $\frac{N_o}{N} = x$, is the average number of monomer units per x-mer molecule

i.e. $x =$ degree of polymerisation.

Now, each pair of molecules which react loses 2 functional groups to form 1 new molecule, i.e. a decrease of 1 in the number of molecules present involves a loss of 2 functional groups. Therefore, the total number of functional groups reacted or lost $= 2\times$ the decrease in the number of molecules $= 2\,(N_o - N.)$

The fraction of functions reacted $p = \dfrac{2\,(N_o - N)}{N_o f}$

which may be re-written

$$p = \frac{2N_o}{f\,N_o} - \frac{2N}{f\,N_o}$$

$$= \frac{2}{f} - \frac{2}{f} \cdot \frac{N}{N_o}$$

but $x = N_o/N$ i.e. $N/N_o = \frac{1}{x}$

Hence

$$p = \frac{2}{f} - \frac{2}{fx}$$

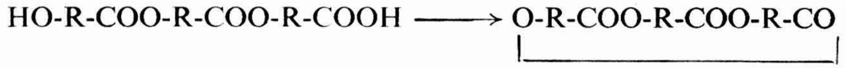
Some comments on the Carothers equation

The reader will recall that, throughout the discussion so far, emphasis has been laid on the *intermolecular* nature of the reactions considered. If *intramolecular* reaction, i.e., ring formation, occurs, the relationships already derived do not hold. This is easily seen in the following example.

The formation of a trimer by intermolecular reaction of 3 molecules of a hydroxy-acid proceeds thus,

$$3\ \text{HO-R-COOH} \longrightarrow \text{HO-R-COO-R-COO-R-COOH}$$

and, as already seen, $p = 4/6$ for $x = 3$. If, now, ring closure occurs by reaction of the OH and COOH groups in the same (trimer) molecule, we have



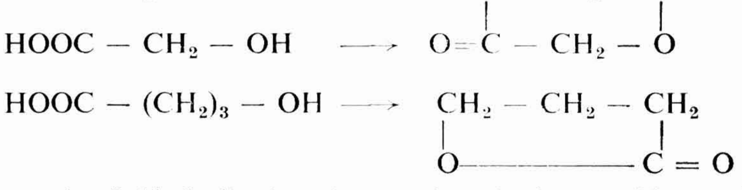
$$\text{HO-R-COO-R-COO-R-COOH} \longrightarrow \text{O-R-COO-R-COO-R-CO}$$

$x = 3$ | $x = 3$

$p = 4/6 = 0.66$ | $p = 6/6 = 1$

Here, an increase in p has led to no increase in x.

This underlines the importance of knowing the chemistry of the reaction before trying to apply functionality theory. Ring formation occurs in many systems alongside intermolecular reaction. It can be allowed for, albeit in a mathematically cumbersome fashion, but it is quite usual to suppose that the extent of ring formation is small in comparison with the extent of intermolecular reaction, and so to ignore it. This supposition is not always justified. In the specific cases when 5- and 6-membered rings can form, the general rule is that they *do* form in preference to intermolecular polymer. Two examples will suffice:



As a result of this facile ring closure, these hydroxy acids are almost impossible to convert into polymers.

The second point here to be made about the use of the Carothers equation concerns the calculation of the functionality of a reaction. This is easy when all reacting species have the same functionality and complementary functions are not involved. Thus, in the formation of polyanhydride from a tetracarboxylic acid, all the monomer units carry 4 (supposedly) identical carboxyl groups and the functionality of the system can only be 4. The situation is just as simple when complementary functions are present in equal numbers, as in the reaction of an equimolar mixture of a trihydric alcohol and a tricarboxylic acid. On the usual presumption that all functions of a given kind are equally reactive, the functionality of this system is clearly 3.

Even when co-reactants are of different functionalities, it is easy to calculate the average functionality to be used in the Carothers equation provided again that, if complementary functions are involved, they are present in equal numbers. Thus, suppose 1 mole of trimethylol propane reacts in polyetherification with 1 mole of ethylene glycol to form a polyether containing residues of both monomers.

1 mole of TMP carries 3 functional groups
1 mole of glycol carries 2 functional groups

i.e. the initial mixture comprising 2 moles contains 5 functional groups and the average functionality is $5/2 = 2.5$.

Similarly, a mixture of 3 moles phthalic acid and 2 moles of glycerol contains a total of 5 moles comprising 6 COOH functions and 6 OH functions. It is in stoichiometric balance and the average functionality per mole is $12/5 = 2.4$. The situation is less simple when the system is not in stoichiometric balance, as in an equimolar mixture of glycerol (3 OH groups) and phthalic acid (2 COOH groups). This situation will be resolved in Part 4 of this series.

Finally, it is necessary to utter a word of warning about the significance of x, the degree of polymerisation. It has already been indicated that this is an *average* value, and the reader will be aware that different sorts of average can be defined when dealing with degrees of polymerisation and molecular weights of polymers. The expressions for x which have been discussed so far have all been derived from a consideration of *numbers* of molecules taking part in the reaction: x is thus a *number* average value. This has important consequences for the way in which the Carothers equation can be applied to practical problems. In particular, it may now be stated that the equation does not accurately predict gelation in a polyfunctional reaction mixture, since gelation is related to *weight* average rather than to number average degree of polymerisation. This matter too will be treated more fully in Part 4 of this series.

Exercises

1. Which of the following systems are in stoichiometric balance? Calculate the functionalities of those that are.
   - (a) Adipic acid 3 moles, trimethylolpropane 2 moles
   - (b) Phthalic acid 3 moles, stearic acid 1 mole, glycerol 2 moles
   - (c) Phthalic acid 2.5 moles, glycerol 1.5 moles, n-butanol 0.5 moles
   - (d) ε-hydroxy caproic acid 1 mole, glycerol 1 mole, sebacic acid 1.5 moles
   - (f) Pentaerythritol 2 moles, trimellitic acid 2 moles, lauric acid 1 mole, benzoic acid 1 mole.

2. Construct a table showing the degree of polymerisation, calculated by means of the Carothers equation, for degrees of reaction 0.2, 0.4, 0.6, 0.8 and 0.9 in the system pentaerythritol 1 mole, phthalic acid 1.5 mole, stearic acid 1 mole.

Answers to Exercises in Part 2.

1. (a) 74/75 or 0.987 (b) 66.7

2. (a) 17.31g. (b) 14.71 g. (c) 94.9 mgKOH/g.
(d) 6.67 (e) $p = 0.9691$, $x = 32.36$.

Hull Section

Reliability of paint testing

A Student Evening was held at the Queen's Hotel, Hull, on 16 January 1969. Mr E. A. Brown, the section Chairman, welcomed those attending and introduced Mr F. D. Robinson, who explained the purpose of the meeting, namely to explore the accuracy and reliability of tests which are continuously made in paint laboratories. On this occasion the measurement of the fineness of grind by means of a Hegmann gauge was used as an example.

About 20 minutes were spent by those present making measurements on three paints which were available, and for this purpose the participants were divided into two groups, those having little or no experience in the test and those who had some experience. All the inexperienced group made tests on the same paint and the more experienced were given the choice of assessing one of the other two paints. The operators were asked to estimate the fineness of the paint tested and to estimate whether their tests were reliable to 0.1 or to 0.25 of a gauge unit.

In the interval, whilst the results obtained were being classified, Dr W. E. Craker outlined some of the considerations involved in determining the best estimate of the true value in a series of tests, taking as examples the determination of viscosity in a Ford 4 cup, and gloss measurement, where error may be involved in making the paint, applying the paint and in instrumental measurement.

Only about ten minutes were available for the discussion of the evening's results. It is intended to hold a further meeting of this kind during this session, at which there will be an opportunity to consider the results more fully.

The evening was considered to be very successful and instructive by all present and it is hoped that it will be possible to publish the results in greater detail in due course. Ten members and 23 visitors were present.

S.R.F.

Newcastle Section

Plastics and some aspects of their pigmentation

On 12 March a lecture entitled "Plastics and some aspects of their pigmentation," was given by Mr E. H. Brook, of British Titan Products Ltd., and was attended by a total of 19 members and visitors. Mr Brook discussed, and produced samples of, the raw materials used in the production of the main commercial types of plastic. He went on to show how differences in these materials and in the manufacturing processes affected the type and amount of pigment required. Slides were shown illustrating the various types of production equipment which could be used to incorporate pigment into the plastic mix. Particular attention was drawn to recent changes which have resulted from the introduction of Easily Dispersible pigments.

A vote of thanks was given to Mr Brook for a most interesting lecture.

D.W.H.

Information Received

(In case of difficulty regarding addresses, members and subscribers to the JOURNAL should apply for details to the Director & Secretary of the Association at the address shown on the front cover.)

British Paints Limited has recently opened a new £500,000 factory at Blaydon-on-Tyne, to manufacture the company's most sophisticated products, including advanced automobile paints, industrial finishes, and advanced elastomeric sealants.

The factory, which occupies a 6½ acre site, with room for expansion up to ten acres, is said to have an initial capacity of about 1,500,000 gallons per year, and this is expected to rise with the change from single shift to round-the-clock operation.

Inertol Company Limited, the specialised coatings division of the **Storry Smithson Group,** has recently issued technical information on *Dinaphon V.103*, a fire retardant compound claimed to meet the requirements of a Class 1 surface when submitted to the surface spread of flame test of BS476 on a plywood substrate.

Dinaphon V.103 is composed of mineral fillers in an incombustible mineral binder. It is said that neither the composition nor the dried coating support combustion, and that the dried coating will not only prevent surface spread of flame, but prevent combustion of the underlying surface.

Inertol have also announced that their London office has been transferred to Leadenhall House, 101 Leadenhall Street, London EC3.

Hangers Paints Limited, the decorative and industrial finishes division of Storry Smithson, has introduced a range of flame retardant paints, similar in use to conventional paints, but which provides a blanket of non-flammable vapour over the paint surface when heated.

Six main types of the paints are available, *Peerless Flame Retardant Flat Paint*, *Floralac Flame Retardant Hard Gloss Enamel Paint*, *Floralac Flame Retardant Undercoat*, *Hangers Flame Retardant Wood Priming Paint*, *Fabriguard Flame Retardant Emulsion Paint*, and *Polyfleck Multi-Colour Paint* (to be used over *Flame Retardant Polyfleck Base Coat*).

A new printer's microscope, specially designed for the printing industry, has recently been introduced by **Gillett and Sibert Ltd.** The microscope can be used to measure accurately the depth of any engraved or etched surface, on flat, curved or cylindrical plates, thus aiding the elimination of greyness, unwanted solids, and fill-up owing to insufficient depth.

It has been announced that **Cray Valley Products Limited** now has available a comprehensive range of booklets describing the uses of *Versamid* polyamide resins. The booklets, entitled "Specifications and compatability data," "Printing inks and heat seal coatings," "Protective and decorative coatings," "Casting and laminating" and "Structural adhesives and sealing compounds," are available from CVP or from **Cornelius Chemical Co. Ltd.**

Lennig Chemicals Limited has recently announced that, owing to increased sales, *Orotan 731* (25 per cent solution) is now available from UK production. *Orotan 731*, an ionic dispersing agent, has previously been available as a 100 per cent solids material, on an imported basis.

Its main uses are claimed to be for dispersing titanium dioxide and inorganic extenders in a wide range of emulsion systems.

"Driers and Drying" is the title of a booklet recently issued by **Hardman and Holden Limited,** dealing with the drying processes associated with surface coatings, with particular reference to the influence of drier catalysts. It is said that the booklet should be of particular interest to younger technologists in the industries.

Technical literature on the cellulose derivatives manufactured by **Wolff and Co.** is now available from **Bayer Chemicals Limited,** which is marketing the products in this country.

Tretol Limited has recently announced a new plastic decorative wall finish. The new product, *Tretol Multiplast*, is a three-coat finishing system, comprising background colour, webcoat and glaze coat. Available in twenty different colour patterns, *Multiplast* is spray-applied, and it is claimed that all three coats can be applied in one day, and that the completed finish resists most chemicals and oils, does not harbour dirt or germs, and is washable.

It has recently been announced that a fourth group will be added to the structure of **Bakelite Xylonite Limited.**

The new group, **BXL Plastics Packaging Group,** will consist of BXL Film Division, to be renamed BXL Flexible Packaging Division, and Cascelloid Division, and will manufacture most forms of plastics packaging, (including film, in bags, sacks and reels, blow-moulded containers and injection moulded closures. Headquarters of the group will be at Blackstock Street, Liverpool.

The results of ten years of research and development work on boron trifluoride amine complexes as curing agents for epoxy resins have recently been published as a technical bulletin by **Anchor Chemical Company.**

The BF_3 complexes range from Anchor 1170 with a curing time of minutes at 50°C to Anchor 1222 with a pot life of months at room temperature. All of the compounds are non-hygroscopic liquids, claimed to be readily dispersible in epoxy resins and to have a shelf life of at least 12 months.

A joint venture by **J. R. Geigy SA** and the **Musashino Chemical Laboratory Company Ltd.** for the manufacture of stabilisers for plastics in Japan has recently been approved by the Japanese government. A new factory will be built close to the Musashino plant in Isohara, Ibaraki province, and the **Musashino-Geigy Company Ltd.** will have its headquarters in Tokyo. Production is expected to commence in 1970.

Laporte Industries Limited has recently announced that, to satisfy the growing demand for hydrogen peroxide in the industries, its capacity for this chemical is to be extended by more than 20,000 tons per annum of 100 per cent equivalent in the UK and Western Germany.

A new booklet on *Dowicide* industrial fungicides and bactericides has recently been published by **Dow Chemical Co. (UK) Ltd.** The products, which are chlorinated and/or phenylated phenols and their sodium salts, are claimed to be effective against fungi, algae, certain viruses and both Gram-positive and Gram-negative bacteria.

A new colour film "The Offset Story," has been produced by **Stanley Schofield Productions Ltd** for the **Coates Group** of companies. The film deals with the invention of the lithographic process and its development up to the present day, including mprovements in machines, paper, plates and ink.

Owing to the continuing decline in the amount of oil seeds processed in the UK, **British Oil and Cake Mills Limited** has recently announced that its Erith, Kent, mill, will close down during the course of the next two years. The run down of the operations will commence in September. The company's Silvertown mill will be unaffected by these changes.

A new extrusion grade of *Breon* rigid pvc, which is claimed to have exceptional resistance to weathering, has recently been developed by **BP Plastics.**

The new compound, *Breon RW 180*, is the result of a comprehensive testing programme, details of which are available from BP Plastics, and is available in white, black, and several shades of grey.

Imperial Smelting Company (NSC) Ltd. has recently issued a folder giving details of the *Isceon* range of fluorochemicals, for use as aerosol propellants, refrigerants, solvents and blowing agents.

A new vinylidene chloride copolymer emulsion, said to make possible the production of gloss emulsion paint, has recently been introduced by **Scott Bader and Co. Ltd.** An illustrated booklet (TL 452) is available from Scott Bader, showing how the product, *Polidene VDC*, can be formulated to produce emulsion paint with a gloss claimed to be higher than many conventional alkyd gloss paints. It is said that no new equipment or new techniques are required for manufacture of the gloss emulsion paints, and ease of application, speed of drying, and lack of residual odour are claimed.

We regret that the new instrument from **Elcometer Instruments Ltd.** referred to in the April issue was wrongly described as the Elcometer Mark III. This should have read the Elcotester Mark III.

Section Proceedings

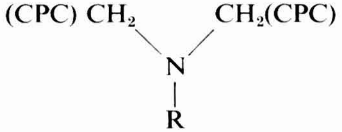
London

The mechanism of action of some deflocculating agents for pigments in paint media

A meeting was held jointly with the Colloid and Surface Chemistry Group of the SCI, on 10 February 1969, at 14 Belgrave Square, London W1. Mr W. Black and Dr A. Topham, of ICI Dyestuffs Division, gave a paper with the above title.

Mr Black said that this work had arisen from a programme of work on the use of surface agents as dispersing agents for pigments in non-aqueous media. This work had shown that there was a high degree of specificity in behaviour. The main class of pigments studied was the phthalocyanines, which presented a major problem. There was a considerable literature on this subject, but one of the main disadvantages was that the agents recommended tended to be used at high concentrations, and consequently they reduced the colour strength of the pigment.

This led to the use of phthalocyanine derivatives, which were found to be highly effective deflocculating agents for pigments in a variety of paint media. These agents were effective with a wide range of types of pigment, i.e., they were non-specific in their action. A chloromethylated phthalocyanine was reacted with an amine, to give a compound of the type $(CPC)CH_2\ N{<}^{R_1}_{R_2}$, where R_1 was H or alkyl and R_2 was an alkyl group. It was also possible to produce polymeric phthalocyanines, of the structure



The adsorption of the diethylamino tris methyl phthalocyanine, $CPC(CH_2{\cdot}N\ Et_2)_3$ on a wide range of pigments was studied. Adsorption was strong from white spirit on a monochloro-copper phthalocyanine, on titanium dioxide, lead chrome, phthalocyanine green, carbon black, and azo pigments, and was also equally strong from a more polar solvent, xylene-butanol. The phthalocyanine derivative was also soluble in aqueous acetic acid/sodium acetate mixtures, and adsorption was pH sensitive, the adsorption increasing with increasing pH. The strong adsorption on many different types of surface was possibly due to the compounds having a large flat molecular structure. It would be possible for these to lie flat on the pigment surface, with their π orbitals interacting, or alternatively the flat molecules could associate at the interface. The area per molecule at maximum adsorption varied from 38Å^2 on phthalocyanine blue to 150Å^2 on a carbon black, based on the nitrogen adsorption surface areas of the pigments.

The effect of these agents, either added during paint milling or pre-coated on a phthalocyanine pigment, was very marked, as judged by a simple brush/pour test. For more detailed investigation, sedimentation volumes of phthalocyanine blue dispersions were measured. These experiments showed a marked interaction between the coated pigments and alkyd resins or model compounds, as judged by the very marked reduction in sedimentation volumes compared with those of the uncoated pigment. From these and other experiments it was concluded that the basic group played an important part in the adsorption of the medium. Cryoscopic measurements indicated a strong interaction between the phthalocyanine derivative and fatty acids, and adsorption measurements showed that adsorption of stearic acid by a phthalocyanine pigment coated with the basic phthalocyanine derivative was considerably greater than by the untreated pigment. Adsorption of 2-ethylhexyl hydrogen phthalate was considerably greater by the coated pigment, and represented about 80 per cent surface coverage.

It had been established that there was no electrical charge mechanism involved in the dispersion of pigments, and the very marked improvement shown was considered to be due to the increased adsorption of resin molecules through their carboxyl groups. These agents were effective in various types of solvent-based paint systems, and in some printing inks. The lack of specificity in adsorption of these compounds was very marked, and this had also been observed with other planar condensed ring systems. Unfortunately, from the point of view of their use with pigments, these condensed ring systems were all highly coloured.

Several points were raised in the subsequent discussion. The area per molecule of the phthalocyanine derivative, at maximum adsorption on copper phthalocyanine, was about 38Å^2, and on titanium dioxide, about 51Å^2. This is surprising because the phthalocyanine derivative would occupy about 120Å^2 lying flat on the surface. If association of the adsorbed molecules occurred one would have expected S-shaped isotherms, whereas the normal Langmuir type were obtained. Desorption experiments indicated that the process was one of physical adsorption and that no ionic bonds occurred. The effect of the type of amine derivative used was significant—an aromatic amine would be less basic than an aliphatic amine and such products were less effective dispersing agents. Those taking part in the discussion included Professor K. S. W. Sing, Dr G. E. J. Reynolds, Dr V. T. Crowl, Dr G. D. Parfitt and Mr A. J. Groszek. A vote of thanks was proposed by the Chairman of London Section, Mr R. N. Wheeler.

The lecture was largely based on work published in full in *Kolloid Zeitschrift* 1966, **213**, (1-2), 150 (In English).

V.T.C.

Insulation coatings in the electrical industry

A joint meeting of London Section with the Organic Finishing Group of the Institute of Metal Finishing was held on 5 March 1969 at the Borough Polytechnic, London SE1. Mr R. Snadow of AEI gave a paper with the above title.

Mr Snadow said that he would be concerned mainly with coatings, e.g., for copper conductors, which would maintain their properties in the mechanical, thermal and chemical conditions to which they would be exposed, rather than with materials of exceptionally high electrical resistance. For simple wire enamels, polyvinyl formal blended with other resins maintained good mechanical properties. Polyurethane enamels were also used; these were self fluxing. Polyesters based on terephthalic acid had better thermal stability, while polyimides could be used at up to 220°C. These wire enamels were applied by dip coating, and the wire was drawn up through a die. As many as ten passes could be used to obtain a film 3-thou thick; multiple coats were preferred to cover up flaws.

Long term ageing effects were of major importance. Generally, where there was one dominant reaction, the Arrhenius equation, $\log L = A + B/T$, could be applied, so then one could predict practical performance by laboratory tests at elevated temperatures. It was found that various materials could sometimes affect one another, and it was therefore customary to make tests on assemblies, which were aged in ovens, with periodic tests of electrical breakdown resistance.

Another class of insulating materials was represented by varnished fabrics, which would be applied to cables, etc. Materials such as alkyds, and polyurethanes were used, sometimes on woven glass fabrics for higher temperature applications. Non-woven fabrics were sometimes used, in composite constructions. Some varnishes were left in the partly cured condition, so that the tapes could be applied to coils and subsequently heated to cure. Bonded micas, for example, on a paper backing were still important, because of the outstanding resistance of mica to electrical discharges. Structures were bonded together with thermosetting varnishes, typically phenolic oil types, or sometimes solventless varnishes were used for high voltage windings. Finally, finishing varnishes were used to give an easily cleanable surface, with good resistance to tracking.

In the discussion, Mr Snadow gave details of the trickle method of application to armatures and similar components. A solventless unsaturated polyester or epoxy resin was used, catalysed just before application. This was trickled on to the heated specimen, which was slowly rotated, and cured very rapidly. Shrinkage was insufficient to disturb the windings, as it occurred mainly before set-up. Cleanliness was essential when applying coatings and this was facilitated by heating to anneal the copper conconductors. The glass cloths used were sometimes heated to provide a clean surface but often aminosilane treated glass was used. Those taking part in the discussion included Messrs I. Zietman, R. H. E. Munn, J. J. Skowron, R. Faiers, G. P. French, S. H. Bell, G. T. Bassett, J. E. Pooley, R. W. Gower and P. M. Varley.

V.T.C.

Manchester

Market research

The Section met at the Manchester Literary and Philosophical Society, on 14 February, under the Chairmanship of Mr W. F. McDonnell, to hear a lecture "Market research" given by Mr D. Clark of English Clays Ltd. In the prevailing adverse weather, only 40 members and guests attended but they were rewarded by a well constructed lecture delivered in a fluent style.

The subject was defined by the lecturer as "the systematic collection and examination of data used to improve profit through marketing." The objective, of improved profitability through improved marketing, was not academic, and although concerned mainly with the future, the past and present were used as stepping stones. The data included observed facts, statistics, estimates and rumour.

A market required definition in terms of size, growth, structure, suppliers, competition, changes in demand and needs. The lecturer remarked that the UK published statistics were generally inferior in quality and quantity to those in North America, and suggested that excessive secrecy and lack of demand were responsible. Unpublished statistics could be acquired by continuous market intelligence surveys, using the technical press and sales reports to give trends and to provide a store of information for specific surveys. A desk search involved such available information, a field search was conducted by the researcher and outside consultants.

From his past experience in N. America, the lecturer considered that few UK Companies were market oriented, and although they spent much on product research, it was unusual to find more than 5 per cent of this expenditure being channelled into market research. Fortunately there were signs that this situation was changing.

Market research could help decisions on expansion, new product introduction, product modification, entry into new markets, acquisitions in unrelated business fields. In the selling field, assistance could be rendered to pricing policy, advertising, publicity and promotional campaigns. Market research could also help in the direction of product research effort.

Finally, the lecturer commented that the approach was prone to error, especially in an alien atmosphere, and while its use would not eliminate mistaken decisions, the probability of these ocurring would be reduced.

An extended and instructive discussion period followed, and finally the vote of thanks was proposed by Mr C. Barker.

D.A.P.

Broad trends in the development of building assembly systems

The second Liverpool meeting of the session was on 14 March at the Building and Design Centre, with Mr W. F. MacDonnell in the chair. A disappointingly small audience of about 30 heard a well delivered and illustrated lecture from Professor D. Harper, of The University of Manchester Institute of Science and Technology, with the title "Broad trends in the development of building assembly systems."

An assembly system used the maximum proportion of large elements prefabricated off-site, complex handling techniques and the minimum use on site of wet processes. A certain amount of pre-assembly was operating in the 18th century and the development of national rail transport aided its growth. The Crystal Palace, built in Hyde Park for the 1851 Exhibition, was an early example of system building, using simple elements of cast iron and glass, and was followed by similarly produced railway stations and glass-houses. A standardisation of design characterises system building, and the similarity of Lancashire cotton mills exemplifies this. Until 1939-45 there was, however, still a large proportion of on-site work, although doors, windows, and some parts of roofs and floors were made off-site. Industrialised building now ranged from little to total factory preconstruction, and involved planned sequences of operations, standardisation, bulk buying and integrated control.

This departure from long established techniques had many causes. Since the war, the industry faced its greatest task ever, with little increase in manpower; a task set not only by the need for replacing the obsolete but also by the demands of an increasingly affluent society. Although using less first class craftsmanship, industrialised building made greater use of semi- and unskilled labour and gave better control over rising losses between inception and project completion. Problems caused by weather and climate were reduced, and the making of large components under factory control led to precision of manufacture. There were some problems associated with the system, apparently verticality was not assured and one lift shaft had been four inches out of true. Industrialised buildings were not yet acceptable to the private buying sector, perhaps because of wide use by local authorities, contractors tended to be under capitalised, and there was some resistance from trade unions.

Although somewhat reluctant to predict the future, Professor Harper could see much greater use of the assembly system but was uncertain if it would attain total use. With the world population expected to double by the year 2000, the task facing the construction industry was formidable, and the effort required in the next 30 years was immensely greater than in the past.

After an interesting question period, the vote ot thanks was proposed by Mr C. Williams.

D.A.P.

Midlands

Inorganic surface coatings

At a meeting held on 21 February at Birmingham Chamber of Commerce, Mr R. J. Cole read a paper entitled "Inorganic surface coatings."

Mr Cole said that the literature on inorganic surface coatings derived from three kinds of sources, namely work on inorganic synthetic polymers, development of new materials for space research and speculative papers on possible developments.

Few organic coatings were stable above 300°C because of the limitations of C-C bonds. Inorganic materials could have superior heat and fire resistance. They were not susceptible to radiation degradation, they were not volatile in high vacuum and they had better colour retention. They were likely to be biologically resistant, since organisms required carbon, but the environment had also to be considered. Depending on the nature of the system they could be non-toxic, since there was no need for toxic mould resistors nor driers.

Inorganic coatings could have very long lives, and had been used for aircraft, space-craft, as solid lubricants, as fire resistant finishes for wood, on buildings, oil tanks and heating equipment.

Inorganic polymers occurred naturally as asbestos and quartz. Glass was made by man as early as 3000 BC. Subsequent developments included silicate coatings, inorganic rubber, silicones and polymers based on C-S, P-N, B-N, B-P and Al-O-Si linkages. Homopolymers of sulphur, phosphorus, selenium and the substituted silicones were known but much more common were heteropolymers with backbones from two or more elements. Melamine could be regarded as an inorganic polymer. Polymers were usually formed by covalent bonding, and crystalline order led to raised melting points. The elements most often encountered were those near to carbon in the periodic table; B, C, N, O, Al, Si, P, S, but others were known and many elements could employ higher valencies by using lower orbitals.

It was possible to introduce organic groups to reduce functionality, alter solubility and wettability, increase stability by steric hindrance and facilitate curing, but thermal stability was likely to be reduced.

The first inorganic synthetic polymer was inorganic rubber, from the action of ammonia on phosphorus pentachloride. It had good heat resistance but readily underwent hydrolysis. Attempts to replace chlorine by fluorine and by hydrolytically stable organic groups had been disappointing.

Diborane was the starting point for various boron-containing polymers. Treatment with ammonia gave borazole, which could be converted into boron nitride, an inert refractory with a structure similar to graphite. Similarly, treatment with phosphine gave phosphoborane.

Zinc dust/silicate systems had been used on satellites. They had excellent heat resistance but were porous and lacked gloss. The pot-life was also short. At the Paint Research Station a silicate paint pigmented with TiO_2 had been developed. It had a good pot-life but was slow to cure. It had good adhesion to aluminium and withstood the bend-test, but adhesion was not so good on steel. Stoving paints based on aluminium polyphosphates had also been examined at the PRS. Hydrated alumina in orthophosphoric acid cured at 200°C to give coatings which were promising for thermal insulation applications.

After the customary discussion period, Mr A. S. Gay proposed a vote of thanks.

L.R.S.

Newcastle

Protective coatings on gas pipelines and storage vessels

The fifth meeting of the present session was held in the Royal Turks Head Hotel, Grey Street, Newcastle, on Thursday 6 February 1969, when Dr J. T. Harrison of the Gas Council presented a paper entitled "Protective coatings in gas pipelines and storage vessels."

The paper described the growth of the Gas Council's pipeline grid for the transmission of natural gas, which would eventually consist of 2,500 miles of large diameter pipe. To cater for load variation, high pressure storage receivers and line packing in storage mains would be used. The problem of laying and commissioning pipelines in the field was illustrated with slides and with a fifteen-minute portion of film extracted from "The methane story."

The policy of coating pipes and storage vessels both internally and externally and the reasons for doing so were described in some detail. The prevention of corrosion processes which could initiate cracks in steel was of paramount importance. Internal coatings on high pressure pipelines were used to increase gas flow characteristics, to minimise dusting problems, to aid pipe cleaning and inspection, to mitigate against fatigue, as well as to prevent corrosion. Each of these points was examined in some detail. The necessary properties of internal coatings were tabulated and the choice of epoxy materials explained.

The main requirements for external pipe coatings were described and included good mechanical strength, good adhesion to the steel surface, high dielectric strength, low moisture permeability and good resistance to soil chemicals and bacteria. The two main types of external coatings used on high pressure lines, hot applied coal tar and extruded polythene, were illustrated together with their application. The effect on the external coating of pressure testing pipelines to yield was described, and experiments carried out at the Engineering Research Station to examine the extent of this problem were mentioned.

In conclusion, the future requirement of the gas industry in the field of surface coating was considered. The speaker thought that powder coatings applied by electrostatic spray and stoved on to the pipe should be given serious consideration. The developments in the USA in this direction were described and comparative costs with other types of external coatings were given.

Dr Harrison then answered questions from Messrs. Watson, Farrow, James and Smith, after which Mr James thanked Dr Harrison for the high standard of the lecture, which was matched by the high attendance and interest shown by the audience.

A.L.

Scottish

Phthalocyanine pigments

On 13 February, at the Whitehall Restaurant, Glasgow, a lecture on "Phthalocyanine pigments" by Dr Pascoe and Mr Harper, of Imperial Chemical Industries, was delivered to the Scottish Section.

Dr Pascoe spoke on the technology and use of such colours. He first outlined the unique properties of the phthalocyanine group and its classification by chemical structure and crystal form, noting that from 6 basic products, over 40 commercial pigments were made for a wide range of end uses. He then went on to discuss three recent developments in detail.

Although an enormous amount of research effort had been devoted to the chemistry of the phthalocyanine group over the last 20-30 years, only recently had a new molecule of technical value appeared, in the form of a phthalocyanine green yellower than previously available. This differed from earlier products based on chlorinated copper phthalocyanine in containing bromine as well as chlorine, the shade yellowing with increasing proportion of the former. Although this effect had been known for many years, it was only recently that it had been made possible to manufacture a product for industrial use with satisfactory brightness and dispersibility.

The speaker then turned to the question of blue pigments for paint, where as well as strength, shade, dispersibility and flow, resistance to crystallisation and flocculation were important. Early crystallisation resistant grades of phthalocyanine blue were followed by modifications giving resistance to flocculation as well, but at the expense of strength, dispersibility and brightness. Later work on surface treatment using small amounts of additives had made it possible to overcome flocculation while retaining these properties unimpaired.

Finally, Dr Pascoe discussed pigments modified to improve dispersibility, which could be made without sacrifice of other properties, e.g. strength. It was believed that the improvement resulted from an open lattice structure of resin in the dry pigment, which was easily penetrated by solvent and collapsed on resin dissolution. Another type of dispersible pigment was that where no structure existed, but a treatment with a surfactant compatible with the medium was used instead. These products were often limited to particular media such as publication gravure, rubber or plastics.

The simplification of paint manufacture made possible by dispersible pigments was illustrated by examples, such as reduction of ball milling times from 16 to 40 hours to ½ to 1 hour, coupled with a possible increase in the mill charge. Similar savings were reported for sand mills (dwell time cut from 10 to 2 minutes) and roll mills (one loose pass instead of two grinding passes). Cavitation and similar mixers were of course ideal for dispersible pigments. Similar advantages in throughput could also be obtained in ink manufacture.

Mr Harper spoke on the physical chemical principles behind recent developments in flocculation resistance and improved dispersibility. The distinction between these was important, flocculation causing strength loss by re-aggregation of a pigment previously fully dispersed, while poor dispersibility prevented proper strength development at any stage.

Flocculation was most severe with α-form phthalocyanine blues, and was originally overcome by the addition of a polar substituted copper phthalocyanine which provided an electrostatic barrier and perhaps encouraged co-flocculation with titanium dioxide. A sulphonic acid group was the commonest substituent, though many others had been used or suggested, and all tended to reduce strength. Theoretical studies had shown that a steric barrier should be more effective and that this could well be provided by adsorbed paint constituents. Adsorption was weak with α-copper phthalocyanine, but could be reinforced by addition of large flat polynuclear molecules which were strongly adsorbed on a variety of surfaces and provided sites for secondary adsorption of paint constituents. Methyl-amino substituted copper phthalocyanines were particularly effective additives, and had also the advantage of insolubility in the media used and hence resistance to bleeding. The mechanism had been tested by comparison of adsorption of stearic acid on to pure copper phthalocyanine and that treated with $\mathrm{CuPc\,(CH_2\,NH}\ \textit{iso}\mathrm{\text{-}Pr)_3}$, when it was found to be markedly higher in the latter case.

Turning to the subject of dispersibility, Mr Harper showed how the drying of aqueous pigment filter cake led to aggregation of particles which necessitated milling before use. This aggregation could, however, be avoided by a hydrophobic coating of, for example, a heavy metal salt of a fatty acid, a reversed orientation surfactant, a wax or resin. Normally, about 100 per cent addition on pigment weight was needed to achieve good dispersibility, but if an open lattice-type structure could be preserved, quantities of additive down to the region of 5-30 per cent of pigment weight were effective. This type of structure was obtained by milling the pigment in an alkaline resin solution, flocculating it by acidification, then heating the slurry above the softening point of the resin and cooling again to harden it in the final structured form.

A lively discussion followed the lecture, further elucidating points made by the speakers. They had so far been unable to demonstrate the lattice structure of dispersible pigments directly by electron microscopy, but deduced its existence from absence of shrinkage on drying, resistance to compressive forces, the very low pigment volume concentration, and especially the need for a softening/hardening stage before improved properties were obtained. These dispersible pigments were not susceptible to overdrying, nor did they contain water entrained in the interstices of the lattice, but had in fact, water contents similar to conventional pigments. Phthalocyanine greens containing fluorine and iodine had been made, but the shade of the former was too blue to be of interest, while the latter lacked brightness and had failed to come up to the standard required in commerce. Bromination beyond the stage found in present commercial greens tended to lead to weakness. It was not expected that phthalocyanine greens would completely replace blue/arylamide yellow mixtures, but usage would increase to avoid metameric green matches. More and more green was being used in car finishes, and growth potential was high.

In proposing the vote of thanks, Dr J. D. Easton complimented the lecturers on their success in presenting matters of interest to specialists and non-specialists alike, and this was carried with applause.

J.D.E.

Notes and News

Register of Members

The following elections to membership have been approved by Council. The Section to which the new members are attached are given in italics.

Ordinary Members

Bibars, Ahmed Abd El Salam, BSc, 7 Abdel Kawi Ahmed Street, Heliopolis, Cairo, UAR. (*Overseas*)

Boam, John Jacob, BSc, 23 Charnwood Drive, London E18. (*London*)

Formoso, Joseph Anthony, BA, 5 Birchwood Road, Marton, Teesside. (*Newcastle*)

Longhurst, Edward Ernest, PhD, BSc, 17 Repton Road, Orpington, Kent (*London*)

McEwan, James Arnold, 30 Hunt Road, Maghull, Liverpool. (*Manchester*)

Panayiotides, Alexander, 27 Keene Way, Galloywood, Chelmsford, Essex. (*London*)

Redondo L. de Arcaute Antonio, Betona-Zona Industrial, Apartado 233, Vitoria, Spain. (*Overseas*)

Rothery, Brian, Wm. Aske & Co. Ltd., 246 Queens Road, Halifax, Yorks. (*West Riding*)

Smith, Albert Pringle, "Lindisfarne," 4 Joiners Way, Lavendon, Olney, Bucks. (*Midlands*)

Spicka, Hynek Anthony Bobby, 37 Pine Gardens, Surbiton, Surrey. (*London*)

Spriano, Paolo, Largo Risorgimento 1, Varese, Italy. (*Overseas*)

Stacchiotti, Domenico, Vitterio Venete Street, No. 26, Sarnice, Bergamo, Italy. (*Overseas*)

Vardon, Michael Edward, 52 Sangley Road, South Norwood, London SE25. (*London*)

White, Bernard Henry, MA, Laporte Industries Ltd., Organics & Pigments Division, PO Box 26, Grimsby, Lincolnshire. (*West Riding*)

Associate Members

Marriott, Peter J., Ivy Bank Close, Sweetloves Park, Bolton, Lancs. (*Manchester*)

Student Members

Chennells, Christopher Ernest, 375 Clontarf Road, Dollymount, Dublin 3. (*Irish*)

Chessman, Thomas Anthony, 69 Seventh Ave., Manor Park, London E12 (*London*)

Coombs, Stuart, 184 Stockport Road, Timperley, Altrincham, Cheshire. (*Manchester*)

Downham, Stephen Airey, 23 Tudor Drive, Kingston-on-Thames, Surrey. (*London*)

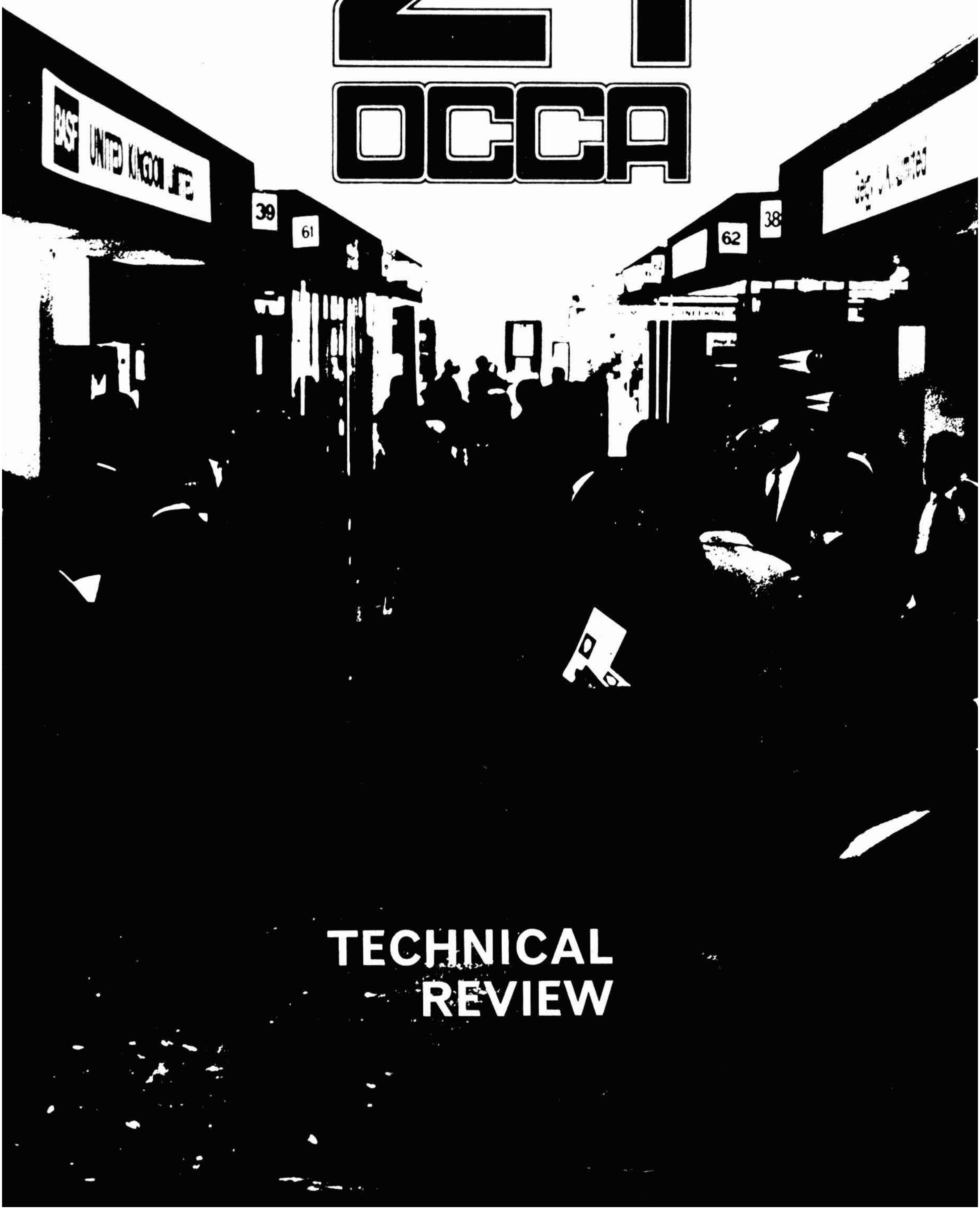
Howarth, John Thomas, Camrex (Holdings) Ltd., PO Box 34, 3 Tatham Street Sunderland. (*Newcastle*)

Redmond, Paul Thomas, 10 Herbert Road, Sandymount, Dublin 4. (*Irish*)

Richards, David Patrick, "Fraoc Ban," Sandyford Road, Dundrum, Dublin 14. (*Irish*)

Seymour, Ian Edward Fenwick, Halls of Residence (Bevis Barbar), Laisteridge Lane, Bradford 5. (*West Riding*)

21
OCCA



TECHNICAL REVIEW

Lord Kings Norton (second from right) on his tour of the Exhibition, with (l-r) Mr A. W. Blenkinsop (chairman, Exhibition Committee), the President (Mr F. Sowerbutts) and Mr R. H. Hamblin (Director and Secretary)

21-OCCA attracts largest number of overseas visitors

Despite difficulties caused by an industrial dispute involving a ban on overtime by standfitters, the Twenty-First Annual Technical Exhibition of the Oil and Colour Chemists' Association held at Alexandra Palace, London, 24-28 March 1969, opened on time. The demand for space by exhibitors was so great that the Exhibition Committee was forced to allocate less than the space requested in a number of cases. Nevertheless, the Exhibition covered a larger floor area than any previous Exhibition.

It was not possible on this occasion to assess the total number attending since it was decided to dispense with the entrance feature (which incorporated electronic counters on previous occasions) in order that all effort could be channelled into work on the stands. Representatives from the 33 countries set out below visited the Information Centre and exhibitors have commented on the large increase in the number of overseas visitors: Argentina, Australia, Austria, Belgium, Brazil, Canada, Czechoslovakia, Denmark, Finland, France, Germany, Greece, Holland, Hungary, Iceland, Ireland, Italy, Japan, Libya, Malta, Norway, Pakistan, Portugal, Rhodesia, South Africa, Spain, Sweden, Switzerland, Thailand, UAR, USA, USSR, Yugoslavia. Among the 160 companies and research establishments showing there were exhibitors from Belgium, Denmark, Finland, France, Germany, Holland, Italy, Norway, Switzerland and the United States of America.

Exhibition Luncheon

The Exhibition Luncheon at the Savoy Hotel, London, was held on Monday 24 March. The principal guest, Lord Kings Norton, was in the company of 250 members, exhibitors and other guests.

In his address of welcome, the President of the Association, Mr F. Sowerbutts, referred to important features in the preceding year's activities of the Association.

This period had covered the 50th Anniversary of the Association and the memorable Jubilee Celebrations. Congratulatory messages received included those from many societies and organisations present on the occasion of this Exhibition Luncheon. The specially bound collection of messages had been seen by overseas sections in South Africa and New Zealand and the newly formed Australian Association, on the occasion of the recent visit to these countries by the President and Mrs Sowerbutts. In his visits to sections in the United Kingdom and overseas the President was impressed by the enthusiasm of members. This enthusiasm was reflected in the organisation of lectures and symposia covering management and other vital topics in addition to those of purely technical subjects.

Mr Sowerbutts referred also to the working parties set up to consider the future of the Association and to study the educational, training and qualification needs in relation to the Industrial Training Act and its implications for the industries served by the Association.

Appropriately, in view of the presence of visitors from overseas, Mr Sowerbutts called attention to the forthcoming Conference "Film formation and curing" to be held at Eastbourne 17-21 June 1969.

Of the Exhibition, Mr Sowerbutts reminded his audience that this was the last to be staged at Alexandra Palace, and on behalf of the Exhibition Committee he thanked the exhibitors for patience and forbearance during years which saw difficulties of siting following a natural and inevitable growth which had earlier proved too great for both Royal Horticultural Halls. Mr Sowerbutts felt certain that the continued support and co-operation of all exhibitors would help and successfully launch the Association's 1970 Exhibition at Olympia.

"This year the Exhibition strengthens still further the link between the Association and London Section" Mr Sowerbutts said, when referring first to the fact that the London Section were responsible for the conception of the first exhibition in 1949 and also the European Liaison Lecture which on this occasion was to be held at Alexandra Palace during the Exhibition.

The last Exhibition was honoured by a visit from members of the Parliamentary and Scientific committee and Mr Sowerbutts reported that the committee had accepted an invitation to attend on this occasion.

In welcoming the guests, Mr Sowerbutts included the Presidents of the British Plastics Federation, Mr G. F. Ashford, Institution of the Rubber Industry, Mr D. B. Collett, the Paintmakers Association, Mr B. Butler, the Plastics Institute, Dr J. E. Sissons, the Research Association of British Paint Colour and Varnish Manufacturers, Mr L. W. Robson, the Royal Institute of Chemistry, Mr L. H. Williams, the Society of British Printing Ink Manufacturers, Mr R. M. C. Nunneley, the Society of Dyers and Colourists, Mr W. G. B. Grant, the Chairmen of the British Colour Makers Association, Mr A. K. Ames, PIRA, Mr R. K. Saunders, the Surface Coating Synthetic Resin Manufacturers Association, Mr B. R. Jenkins, the London Section of the Association, Mr R. N. Wheeler, the Master of the Worshipful Company of Painter-Stainers, Mr J. Nicholson, the Vice-President of the Society of Leather Trades Chemists, Dr F. H. Kroch, the Immediate Past President of the Institute of Metal Finishing, Mr E. L. Masek, the Directors of the Paintmakers Association, Mr K. S. Flory, the

Paint Research Station, Dr G. de Winter Anderson, PIRA, Dr G. L. Riddell, and the Hon. Secretary General of the Institute of Metal Finishing, Dr S. Wernick.

Mr Sowerbutts then extended a special greeting to the Guest of Honour, Lord Kings Norton, and referred to his career in the Civil Service and subsequently in prominent companies in the coatings industry. Lord Kings Norton's particular activities in education were of great interest to the Association since he is Chairman of the Council for National Academic Awards.

Lord Kings Norton in his reply was clearly in harmony with the Association's endeavours in the world of education and training and he recounted his part in the evolution of degree level awards for students of technical colleges who achieved the necessary standards. He went on to refer to the growth of sandwich courses and increased recognition of the value of simultaneous education for the academic and practical parts of a profession and subsequently to the changing attitudes to higher education in scientific and, particularly, technological fields. Lord Kings Norton was glad that the Association was alive to the merits of the sandwich course and hoped that the working party would look hard and long in that direction.

The official opening was performed at Alexandra Palace at 3 p.m. by Lord Kings Norton, who afterwards toured the exhibition in company with the President, the Chairman of the Exhibition Committee, Mr A. W. Blenkinsop, and Mr R. H. Hamblin (Director and Secretary).

Technical Report

Technical Education

The theme of the Technical Education Stand was "Polymer chemistry in paint" and a leaflet was available which explained how a liquid film-former can be designed from simple molecular units and how resultant properties of the film of paint can be deduced from the arrangement of molecular structure. The building of larger structures and some of the familiar polymers were described together with the relationship of these polymers and different types of paint. The stand illustrated the descriptive leaflet by molecular diagrams and models of four polymers used in paint formulations, and dynamic models illustrating the effect of cross-linking on the properties of polymers. The equipment for the molecular models was kindly supplied by Catalin Ltd.

Research Associations

The PAINT RESEARCH STATION demonstrated the Telcomp Computer Terminal and gave information on the PRS programmes. The service is available to members for evaluation of computer applications to their own problems and for data processing. Programmes include colour matching and physical properties of coating systems including rheological studies.

Technical Journals

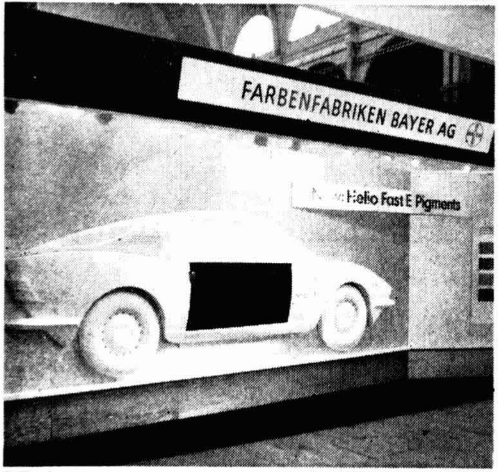
PAINT OIL & COLOUR JOURNAL, the weekly trade journal, demonstrated its reporting of new developments. Also available on the stand were other publications from the Scott Greenwood sales department.

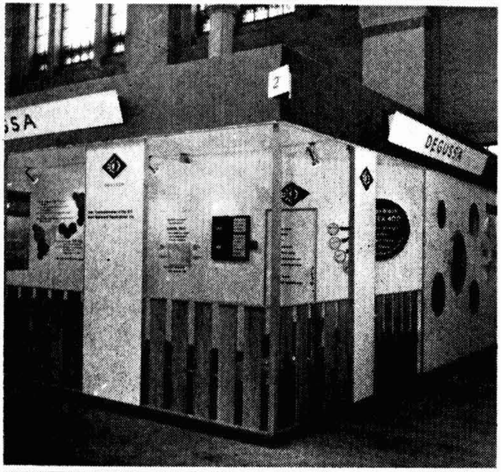
PAINT MANUFACTURE showed recent examples of its technical presentation.

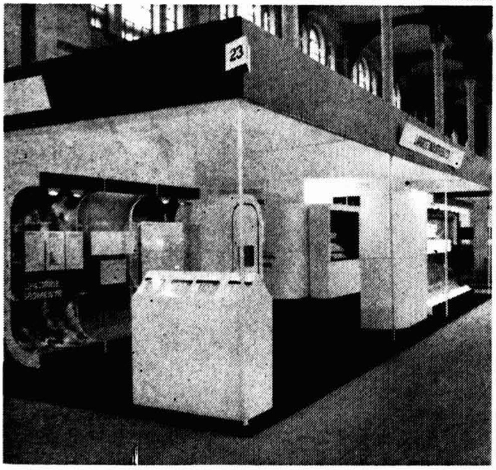
PAINT TECHNOLOGY showed the range of journals and directory covering coatings and related manufacturing and user interests.

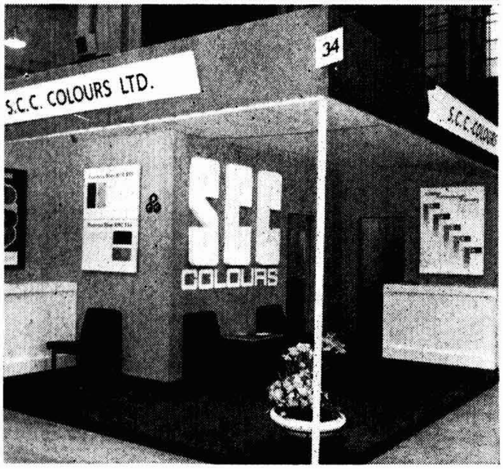

88
KRONOS TITANIUM PIGMEN
FORMATION
KRONOS
Optical
Perfor
KRON
Pigme


AMATED OXIDES 1939 LTD.
AMALGAMATED OXIDES 1939 LTD
MORRIS
ASHBY


FARBENFABRIKEN BAYER AG
Helio Fast E Pigments


SSA
2
DEGUSSA


23


S.C.C. COLOURS LTD.
34
S.C.C. COLOURS
SCC
COLOURS

Pigments

ALLIED CHEMICAL CORPORATION introduced an extremely transparent ferric hydrate lake, *Gold Powder Lake YL.8753*, giving gold shades with aluminium powders. Blends of this new pigment with *Harmon* quinacridone and perylene pigments illustrated the use in automotive colours. AMALGAMATED OXIDES showed the use of dry powder silicates with zinc powder in anti-corrosive paints, a continuation of work carried out since the last exhibition. The *Morris Ashby* products on this stand included titanium dioxide pigments and *ED* types of red oxide: *ED7* and *ED9*. BASF (UNITED KINGDOM) LTD introduced new pigments of excellent light fastness and durability; *Paliotol Yellow 4G* and *Paliotol Red 3G*. Two new blue-shade red pigments, *Paliogen Maroon GL* and *Paliogen Maroon 2BL*, intended for use in high quality industrial coatings, were shown.

BRITISH TITAN PRODUCTS CO. LTD. illustrated results of Arizona exposure tests on the chloride process pigments *R-TC2* and *R-TC6* and included comparisons of their Carlton and Florida exposures. Two new durability scales were introduced, a chalk index and a gloss life index in thermosetting acrylics. Effect of pigment and amount of dispersants on the properties of latex paints were displayed and results of a very comprehensive study of the effect of extenders, coalescing agents and type of pigment were included.

CIBA CLAYTON LTD. demonstrated the use of a new dioxazine pigment, *Cromophtal Violet B*, and claimed advantages over the carbazole derivative. Tests in acid industrial atmospheres showed the superior behaviour of the *Cromophtal* red pigments and new additions to the *Microlith* ranges of pre-dispersed pigments were introduced. COLUMBIAN INTERNATIONAL (GREAT BRITAIN) LTD. concentrated on pigment dispersions including zinc resinate chips for printing inks. Carbon black dispersions were also featured by DEGUSSA, who also introduced *Printex 400*, a pigment with blue tone and high strength, giving good flow and gloss.

FARBENFABRIKEN BAYER AG gave advice on the use of their titanium pigments *R-KB-2*, *R-KB-3*, *R-FD-1*, and *R-D*, demonstrated *Iron Oxide Black 303T* as a heat-stable, non-magnetic pigment and showed three new *Cadmopur* types, *15 GS*, *S*, and *BS-F*. The *Helio* fast red "*E*" range is now augmented by five additional pigments.

GEIGY (UK) LTD. gave individual displays for each industry; plastics, paint and ink were served well by graphs and panels depicting properties of pigment and included the new *Brown CB* for plastics, a development product of the *Irgazine* type, *Pigment Yellow GF 08217* for paints and several pigments for printing inks including the development *Red L2B* for easy dispersion, and development *Pink FB2*, an economic copper ferrocyanide type.

HOECHST UK LTD. introduced the new light fast pigments for plastics; *Yellow 3G* and *Red GG*. The full *Hostaperm* range was shown for pale tint automotive finishes and included the new *Hostaperm EGVP*. An important introduction for non-toxic inks and paints is *Permanent Yellow NCG-O* which was compared with a chrome yellow. The *Colanyl* range of pre-dispersed pigments was shown to have outstanding wet rub resistance when used in aqueous flexographic inks. A permanent yellow of improved transparency and gloss, *DHG transparent 01* was shown.

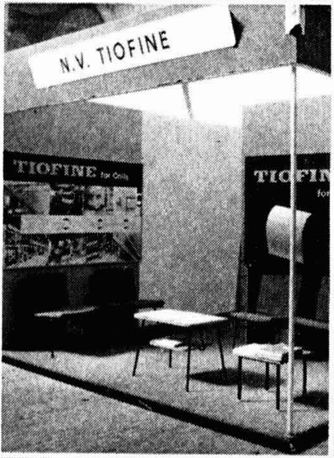
IMPERIAL CHEMICAL INDUSTRIES LTD. exhibited further developments and additions to their range of *Easily Dispersed* pigments. INDUSTRIAL COLOURS LTD. gave excellent product information and technical advice on the use in all types of inks and certain types of paints and plastics of their ranges of *Flare* fluorescent pigments: *Flare 600*, an improved range for paints inks and plastics, a pre-dispersed series, *Flare 610*, for the same use, *Flare 630* for letterpress and gravure inks, and *Flare 800* for lacquers, flexo, gravure, and plastics.

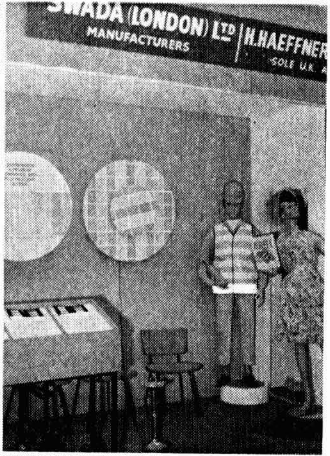

yl Products Ltd
21


UNITED COKE & CHEMICALS CO. LTD.
89


KOLLMORGEN (U.K.) LTD.
MACBETH
+
DAVIDSON & HEMMENDINGER
+
INSTRUMENT
KOLLMORGEN
(U.K.) LIMITED


FORMERLY E. HUNT & CO. LTD.


N.V. TIOFINE
TIOFINE
TIOFI


SWADA (LONDON) LTD
MANUFACTURERS
H. HAEFFNER
SOLE U.K.


HESS CHEMICALS LTD.
ARMO


Dr MEAZZI
VIBRO-MAC (ITALY) Dr MEAZZI
VESSEL CLEANING EQUIPMENT
sieving machines
diaphragm pumps
stirrers


NORSK S
SPRÆNGSTOFINDUSTRI A/S

New additions to their various pigment dispersion ranges were introduced on the stand of INTERNATIONAL COLLOIDS LTD. KINGSLEY AND KEITH (CHEMICALS) LTD. showed the new alkali blue pigments of the *Sherwin-Williams Co.* and the *Ellis Jones Rubine toner 3B.*

KRONOS TITANIUM PIGMENTS LTD. included the improved dispersibility of *RA61* in their display and gave information on tint formulation and exposure tests using different grades of their pigments. LAPORTE INDUSTRIES LTD. illustrated their range of sulphate process titanium pigments and included the new *RE36*, a specially suitable aqueous system grade. Properties of chloride process pigments were indicated and presaged the introduction of such a pigment by this company. SACHTLEBEN AG and PIGMENT CHEMIE GMBH gave technical information on a full range of titanium dioxide pigments.

On the stand of SCC COLOURS LTD· three phthalocyanine blues were highlighted: *Fastona Blues GR*, *RFR*, and *RNC*. Three new quick-dispersing rubines were shown, namely *92267 QD (4BCT)*, *92147 QD (4B)*, and *9543 QD (6B)*. This last mentioned pigment is the bluest and recommended for Kodak Process Magenta. In addition to a display of Florida exposures of enamels based on lead chromes with less than five per cent soluble lead, a new anti-corrosion pigment, zinc chromate phosphate, was introduced. A new range of copper ferrocyanide pigments was stated to be particularly suitable for water based inks. SPELTHORNE METALS LTD. showed the effect of pigment and vehicle factors in influencing rust inhibition of metallic lead based primers. NV TITAANDIOXYDEFABRIEK TIOFINE showed the use of *Tiofine R40* in coil coatings. VUORIKEMIA OY claimed higher brightness and improved dispersibility for their coated titanium dioxide pigments and gave an account of recent developments which included a range with organic coatings in addition to those with inorganic coatings.

Extenders

The range of *Aerosils* exhibited by DEGUSSA included the strongly hydrophobic *Aerosil R972*, conferring water-resistance to paints and lithographic inks. This company also displayed examples of anti-setting and matt properties of *HK 125*, *TK 500* and *OK 142*.

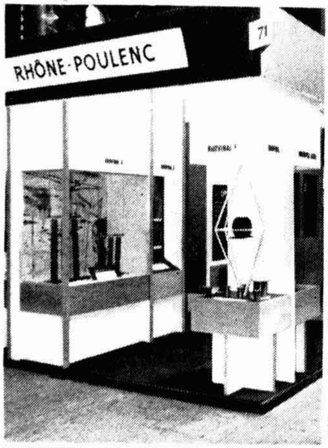
The use of china clay extenders from English China Clay Sales in alkyd flat paints was illustrated by KINGSLEY AND KEITH (CHEMICALS) LTD. Work on primers and textured paints has been continued by NORWEGIAN TALC (UK) LTD. and the use of talc in these developments was illustrated on their stand.

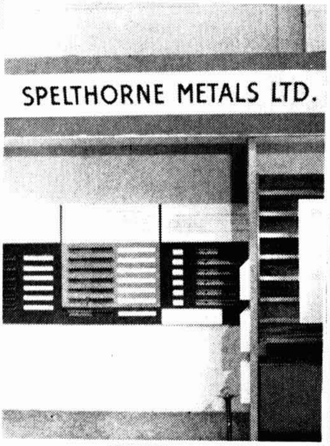
Oils

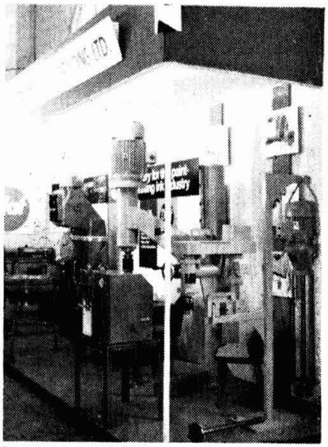
CHEMISCHE WERKE HUELS AG prominently featured two important development products, *BL801* and *BL803*, both 1, 4-cis polybutadiene oils. These low viscosity materials enhance the oxidation drying of oils and alkyds, and examples were shown which included the replacement of a third of the fish oil fatty acid, resulting in an alkyd with drying time reduced from 25 to 7½ hours. *BL 803* is claimed to be ideal for use in oil-based primers without impairing oil penetration.

One of the most interesting new developments was a silicone modified polyurethane oil featured by HAROLD HEYDON & CO. LTD. Another new type of urethane oil was included in the display of SCADO-ARCHER-DANIELS NV. This oil has favourable non-yellowing properties and is intended for primers and also for finishes.

Developments in the field of emulsifiable drying oils were featured by YOUNGHUSBAND STEPHENS & CO. LTD. These included emulsifiable stand oils, enamel, dehydrated castor oils and one under the trade name *Rothersol* for water dispersible printing inks.


71
RHÔNE-POULENC


SPELTHORNE METALS LTD.


LTD.


New for the printing ink industry
NEW


SYNTHESE N.V.
S


43
LTD.


53
SCHOLVEN-CHEMIE AG
MEMBER OF VEBA GROUP
-CHEMIE AG
SCHO


84
NTS (SALES) LTD.
SHEEN INSTRUMENTS (SALES) LTD.
SHEEN


VICTOR WOLF LTD.
Limited
England

Resins—alkyds (drying oil modified)

A thixotropic alkyd, *Alkydol F22*, which allowed spraying of thick coats, was shown by FARBENFABRIKEN BAYER AG. Silicone alkyds as a constituent of air drying paints of low distention, in spite of lower chalking rates than conventional alkyds, were emphasised in the exhibit of HAROLD HEYDON & CO. LTD. Urethane alkyds were featured by PLASTANOL LTD. with *Hythanes 1*, *2* and *3*.

Resins—alkyd (plasticising)

FARBENFABRIKEN BAYER AG showed a special alkyd, *Alkydol R26*, for use with highly reactive melamine in formulation of 80°C enamels giving films of high surface hardness, good colour retention, gloss-retention and improved alkali resistance.

J. H. LITTLE & CO. LTD. illustrated three new alkyds, a coconut type H45 and two oil-free alkyds, *Linoplasts AL 90601*, based on isophthalic acid, and *AL 9060* based on phthalic acid. Both are recommended for use with melamines. When higher pigmentation and high temperature colour retention are required these materials are claimed to be superior to acrylics. W. A. MITCHELL & SMITH LTD. have developed improved non-drying alkyds, *Mitchalacs 241* and *261X*, intended for non-yellowing stoving finishes giving toughness and gloss. NORSK SPRAENGSTOFINDUSTRI A/S exhibited *Dynotal T-36X*, a new short oil alkyd based on tall oil, having curing properties and recommended for use with *Dynomin V1-16*.

Resins—amino

BIP CHEMICALS LTD. demonstrated a method for determining the evolution of formaldehyde following the drying of acid catalysed UF resins. FREDK. BOEHM LTD. introduced a new high reactive melamine resin, *FM 502*, having very good compatibility with thermosetting acrylics and showing versatility in curing performance. CIBA (ARL) LTD. had a methoxylated melamine/formaldehyde resin, *Citamin ML 1000 GB* for use in water or organic solvent systems for cross-linking epoxy resins and esters, alkyd, acrylic and polyester resins. Wider compatibility and harder films than traditional MF resins are claimed.

Dynomin U1-16 is a new isobutylated urea formaldehyde resin included in the exhibit of NORSK SPRAENGSTOFINDUSTRI A/S. This resin is suitable for acid catalysed finishes for curing at room temperatures and at elevated temperature. It can also be used without catalyst in stoving finishes.

Resins—polyamide

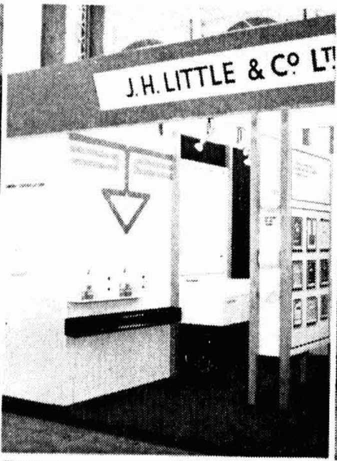
A new ethanol reducible polyamide resin, *Versamid 754*, was featured by CORNELIUS CHEMICAL CO. LTD. and recommended for use in flexographic and gravure inks and for overprint varnishes. Low odour, high gloss and good adhesion to a wide range of plastic films is claimed. VICTOR WOLF LTD. introduced two new resins for the printing ink industry.

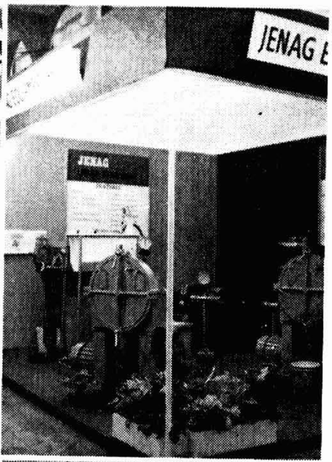
Wolfamid 15 is said to give better water resistance, grease resistance, and improved alcohol solution stability than the *Wolfamid 6* from which it is derived. Another modified version of *Wolfamid 6* is the *Wolfamid 16* having enhanced properties and particularly when used with *RS* or *SS* grades of nitrocellulose. In addition to improved film properties *Wolfamid 16* is claimed to show excellent pigment wetting, low viscosity and fast solvent release.

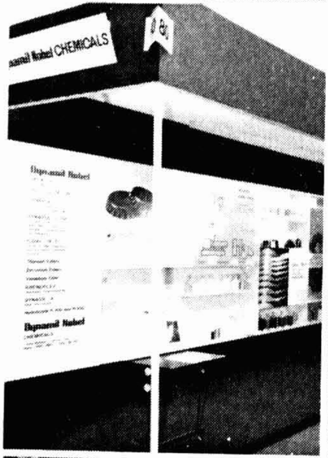
Resins—unsaturated polyesters

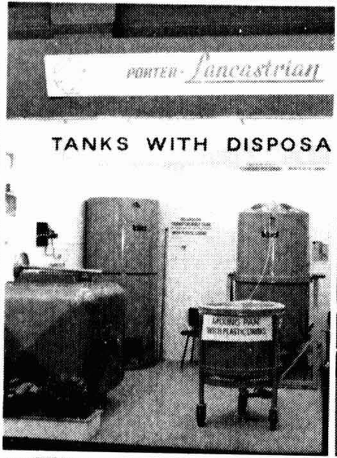
VICTOR BLAGDEN & CO. LTD. in their display, gave emphasis to the *Cargill silicone polyester 6103*. DYNAMIT NOBEL CHEMICALS displayed *Dynapol®* *L202* and *L203*, thermoplastic polyesters based on terephthalic acid, particularly

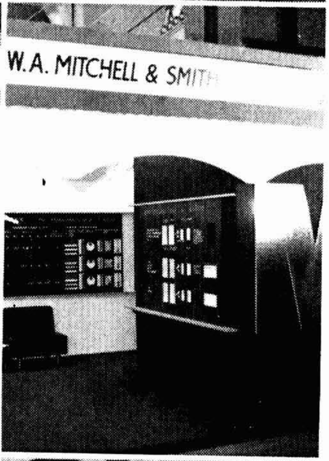

47

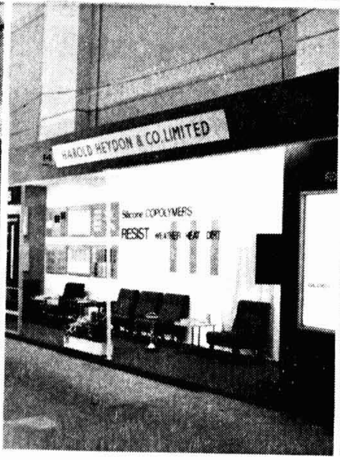

J.H. LITTLE & C° LT

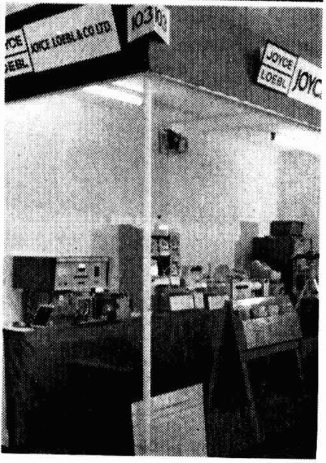

JENAG E
JENAG


namil Nobel CHEMICALS
Dynamit Nobel
Dynamit Nobel


PORTER-Lancastrian
TANKS WITH DISPOSA


W.A. MITCHELL & SMIT


HAROLD HEYDON & CO. LIMITED
Silicone COPOLYMERS
RESIST WEATHER HEAT DIRT


JOYCE LOEBL
JOYCE LOEBL & CO LTD.
103
JOYCE LOEBL
JOYC

suited for the manufacture of binding agents for lacquers and printing inks. Lacquers based on these binders are said to exhibit excellent adhesion to many substrates without pretreatment and also show good elasticity. They can be punched and deep drawn and are particularly suitable for roller coatings. Other applications are for printing on plastic films and sintering powders for electrostatic and fluidised bed coating techniques. Films from *Icdal® TE* and *Icdal® TI* give resistance to high temperatures.

Resins—Epoxy

CIBA (ARL) LTD. showed a modified liquid epoxy resin *X83/342* for solvent-free coatings and seamless flooring applications. High impact strength and good flexibility are claimed. A low viscosity hardener *X83/341* is recommended where pale colour and colour stability are important. Solutions of high molecular weight epoxy resins were also featured; *X83/218* in 2-ethoxy ethanol acetate and *X83/248* in methyl ethyl ketone. These solutions can be linked with amino and phenolic resins or with diisocyanates. Suggestions for use in air-dry enamels, zinc-rich primers, pretreatment primers, clear lacquers, and in one-pack prefabrication primers were given. SHELL INTERNATIONAL CHEMICAL CO. LTD. presented information on the formulation of new water soluble resins suitable for primers applied by electrodeposition.

The excellent lath stability of this resin, *Epikote DX31*, and the high corrosion-resistance of the stoved films were demonstrated. The use of epoxy resin *828* in conjunction with *Epicures 102*, *103* and *104* as curing agents for hot spray solventless finishes was also featured for the first time. Thick, high gloss coatings on an asbestos cement substitute demonstrated the potential of these materials. With *Epicure 103*, a highly reactive polyamine, curing down to 0°C was possible. ANCHOR CHEMICAL CO. LTD. showed a new curing agent for epoxide resins and claimed low odour and effectiveness at low temperatures and under water.

Resins—acrylic

BASF (UNITED KINGDOM) LTD. exhibited several new thermosetting acrylics intended primarily for surface coating applications. *Larodur 8220/1* is a low priced, chemical resistance acrylic formulated for use in domestic appliance finishes. *LR 8198* is recommended for use in automobile top coats and is capable of re-flow. *LR 8195* and *LR 8196* are both hydroxy-functional acrylic polymers which may be cross-linked with polyisocyanates and examples of the use of these polymers were shown, including floor varnishes and coatings for metals, asbestos and plastics. *LR 8259/1* is an acrylic polymer which has been designed for use in powder coatings. This material is self cross-linking although it is recommended for use with epoxy resin.

BP CHEMICALS (UK) LTD. showed the use of their hydroxylated acrylic *Epok DZ 106* with a fast curing isobutylated melamine/formaldehyde resin *N9195* in reflow acrylic enamels.

Resins—emulsion polymers

BP CHEMICALS (UK) LTD. showed further evidence of the usefulness of *Epok V8300* introduced at last year's exhibition and a *VeoVa*/vinyl acetate copolymer *V8400* for best durability and alkali resistance. BUSH BEACH & SEGNER BAYLEY LTD. introduced *Vinnapas* dispersion *CF25/11*, a vinyl acetate/vinyl laurate/vinyl chloride terpolymer, and among other resins on this stand were the range of pvc-pva resins manufactured via a suspension polymerisation technique.

Vinnol VH15/45 and *VH15/50*, useful in paint coatings for better adhesion and water-resistance.

Styrene-butadiene polymers *Litex F* and *Litex D*, used in exterior paints, were illustrated on the stand of CHEMISCHE WERKE HUELS AG, who also showed

Attendance at the Exhibition was once again high, and the value of the central seating area was shown by its constant use

vinyl co- and terpolymers and illustrated their properties with a dipping primer based on *Vilit MC* (containing free hydroxyl groups). Other resins included a special styrene free polyester resin *LTH*. KINGSLEY AND KEITH (CHEMICALS) LTD. showed the *Ubatol* range of polymer emulsions including *Ubatol U 7401*.

Acrylic emulsions shown by LENNIG CHEMICALS LTD. included *Primal AC-490*. RHONE POULENC/REDIS introduced a vinyl acetate/maleic copolymer emulsion, *Rhodopas 5000M*, with good flexibility and low temperature film-forming properties. *Rhodopas AE 800*, a vinyl acetate/ethylene copolymer emulsion having high flexibility, curing below 0°C and giving good alkali resistance, was illustrated by a continuously running flexing test.

VINYL PRODUCTS LTD. displayed the latest data on new paint compositions and weathering tests based on new emulsion media. Results of work on existing resins such as *Vinamul 6700* were included. New resins such as *Vinacryl 4172* representative of a range of styrene/acrylic emulsion copolymers were demonstrated as having good pigment binding properties, resistance to alkali, water and UV light, good flexibility and low dirt pick-up tendencies. Brushable semi-gloss and lustre paints based on *Vinamul 6840*, an alkali activated emulsion based on a vinyl acetate-acrylic copolymer was also featured.

Resins—miscellaneous

FREDK. BOEHM LTD. & HERCULES POWDER CO. featured the use of *Terpolyn* resins in hot melt and pressure sensitive adhesives and the result of recent laboratory work on the uses of Zn/Ca resinate as additive to Neoprene adhesives. A relatively new resin, *Pioneer RP3* was displayed as a vehicle for heat-set web-offset ink having good solvent release.

UNION CARBIDE EUROPE SA introduced an advance in resins for solution coatings involving two co-reacting resins, *VMCA* and *VERR*. High solids contents can be achieved with these resins, which have a high tolerance for aliphatic hydrocarbons. CIBA (ARL) LTD. have a modified phenolic resin solution, *X83/486*, used as a curing agent for epoxy resins and designed to produce high chemical resistance films when cured between 60°C and 90°C. LAPORTE INDUSTRIES LTD. showed a new ketone resin *CROF 110*, distinguished from existing resins in the range by its alcohol solubility. Improved resin /modified phenolic resins for printing ink were exhibited by W. A. MITCHELL & SMITH LTD., these are *Mitchanols 30*, *34* and *37*. UNITED COKE & CHEMICAL CO. LTD. gave information on the performance of their improved pale coloured *Dipol* pitches.

Chemical intermediates

AMOCO CHEMICALS EUROPE gave prominence to polyfunctional acids and esters used as resin components. Data were available on a new dibasic acid *PIDA* claimed to impart heat and chemical resistance to alkyd resins. *PIDA* is 1, 1, 3-trimethyl-5-carboxyl-3 (para-carboxyphenyl) indan.

KINGSLEY & KEITH (CHEMICALS) LTD. exhibited two acrylic monomers. *Blemmer G.*, glycidyl methacrylate, is for use in acrylic resins giving improved hardness, gloss and gloss retention. *Blemmer PP200*, polypropylene glycol mono methacrylate, is recommended for use in thermosetting acrylic systems giving improvement in flexibility and retention of flexibility on ageing.

SHELL INTERNATIONAL CHEMICAL CO. demonstrated the use of *Cardura E* in the preparation of oil free alkyds.

VICTOR WOLF LTD. introduced iso-oleic acid containing up to 80 per cent mono unsaturation and virtually free from dienes. *MOSA* (Methyl-oleyl succinic anhydride), a development product containing an anhydride and an ester group is trifunctional and has particular application in polyesters and polyamides.

Also exhibited was a newly developed product in the dehydrated castor oil fatty acid range with a high concentration of trans/trans conjugated linoleic acid.

Additives, driers, surfactants etc.

KINGSLEY & KEITH (CHEMICALS) LTD. displayed *Metatin* fungicide and bactericides. BERK LTD. gave new information on *Bentone* gellants and introduced a new grade, *Ben-a-gel EW*, for use in emulsion paints. Information on the use of

Members of the London Section Committee, joined by the President and the Chairman of the Exhibition Committee, with the speaker before the European Liaison Lecture. (L-r) Mr R. N. Wheeler (Chairman), Mr R. H. E. Munn (Hon. Secretary), Mr D. G. Soar, Mr A. W. Blenkinsop (Chairman, Exhibition Committee), the President (Mr F. Sowerbutts), Dr K. H. Frangen (Lecturer), Mr J. E. Pooley (Vice-Chairman), Dr V. T. Crowl (Hon. Publications Officer), Mr D. E. Eddowes (Hon. Programmes Officer), Dr H. R. Hamburg (Hon. Treasurer)

various bactericides and fungicides were available. BRITISH CELANESE LTD. illustrated development work incorporating *Celacol* and *Courlose* products. BUCKMAN LABORATORIES INC. introduced *Busperse 53*, an anti-foamer and de-aerator, and *Busorb 30*, a low cost ultra-violet light absorber. Existing products *Butrol*, a paint preservative, and Busan 11M1, aiding resistance to corrosion, fire, fungus etc., were emphasised through additional information from recent work. FREDK. BOEHM LTD. and HERCULES POWDER CO. LTD. have available *Klugel*, a hydroxypropylcellulose ether which is soluble in water and in organic solvents. IMPERIAL CHEMICAL INDUSTRIES LTD. showed *Neofas 670*, which gives efficient thickening at low cost and incorporates the desirable features of good flow and levelling. LAPORTE INDUSTRIES LTD. demonstrated *Laponite*, a clay mineral, and showed its utility as a viscosity stabiliser when used with cellulose thickness in emulsion paints. Organic titanium compounds were also shown. NOVADEL LTD. gave information on a number of new products including *Siccatol V*, a new vanadium drier for use with polyurethane oils and alkyds, *Siccatolic acids 46B* and *64B* for production of new non-drying alkyds, *Nouryflex 115* and *Nourypol*, newly developed polyols for use in solvent free polyurethane systems. *Nouryset TWS*, a water soluble acrylic stoving medium, and a new curing agent, *SHO-Amine X*, were also presented.

TITANIUM INTERMEDIATES LTD. showed effect of pH on gel strength of latex paints containing alkanolamine titanates used with various thickness. UNILEVER-EMERY NV featured *Empol 1022*, a modifier for powder coatings based on epoxy resins, giving improved flow and non-caking characteristics.

Empol 1010 is a new very pale dimer acid with low unsaturation. *Emery 3020*, a development product, which is a dimer acid with even lower degree of unsaturation, was also shown.

Solvents

CARLESS CAPEL & LEONARD LTD. introduced a new deodorised high boiling petroleum fraction, *Paraset 29*, intended for low odour printing inks for food wrappers etc. IMPERIAL CHEMICAL INDUSTRIES LTD. featured *Aromasol N*, a petroleum aromatic solvent consisting of a mixture of C9 hydrocarbons. This solvent has low odour, low sulphur content and excellent solvent characteristics. Solvent recovery was emphasised in a display by LANCASHIRE TAR DISTILLERS LTD.

The theme of the Technical Education Stand was "Polymer chemistry in paint"

Manufacturing equipment

AMF INTERNATIONAL LTD. introduced a new stainless steel casing for their existing filters, thus facilitating filtration of water-based materials. *Model V1U* universal mixer kneader with worm extrusion discharge for stiff paste was also shown. BEKEN ENGINEERING LTD. showed their new British made sandmill and a laboratory duplex mixer. WILLIAM BOULTON LTD. featured a new mixer for paint blending under vacuum and a new *Vibro-Energy* shear mill to speed dispersion and finishing in a single operation. CONTROSION LTD. demonstrated the operation of the *Series 3000* equipment for electrostatic spraying of powder or liquid, also *Model 3008* paint test equipment. D. H. INDUSTRIES LTD. gave full detailed description and demonstration of their automatic filling line. DIAF A/S showed a filling machine, *Viscofil*, operated by compressed air. HYGROTHERM ENGINEERING LTD. introduced the *Caloric* burner system based on the *Hygrotherm R* high intensity burner and a simple resin cooler wherein resin is cooled by a jet of air as it is transferred to a moving belt. JENAG EQUIPMENT LTD. exhibited a number of special strainers. A range of triple-roll mills including small machines and two East German mills from UNITECHNA were shown by MARCHANT BROTHERS LTD. who also demonstrated a laboratory coater capable of coating panels at speeds ranging from 3,500 to 11,000ft per hr.

MASTERMIX ENGINEERING CO. LTD. featured variable high speed stirrers ranging from laboratory size upwards, 1,000 gallon capacity models being available, and a high torque disperser for use with very heavy pastes and putties. A wide range of bead mills with interchangeable grinding shells was also on show.

MILLROOM ACCESSORIES & CHEMICALS LTD. introduced the *Biotomix*, a mobile mixing and dispersing unit which is claimed to be effective in high-viscosity materials through its novel action. MOLTENI OFF MECC also included laboratory models including the *Microsfera* continuous grinder available up to 55 gallons in production models. PREMIER COLLOID MILLS LTD. emphasised the portability of their range of mixers constructed in light alloy and demonstrated the *Dispersator* head that can be fitted to the stirrers. PETER SILVER & SONS LTD. included their new flameproof machine with built-in flameproof switch. SILVERSON MACHINES

LTD. displayed the *Multi Shear* mill, a new machine available in 50 hp and 100 hp sizes, and the Silverson *Flash Mix* unit for rapid dispersion of small quantities of powder in large quantities of liquid. HERBERT SMITH & CO. (GRINDING) LTD. exhibited two additions to the *Vortexion* range. TORRANCE & SONS LTD. demonstrated improvements in their well-known cavitation dispersers, *Microflow* and paste mixers.

PORTER-LANCASTRIAN LTD. showed methods of storing paints and tints in air free conditions, using the *Portatank*, a tank with disposable lining. By storing in air free conditions, it is claimed that skinning and build-up of solid is eliminated.

VIBRO-MAC sas OF E MEAZZI & CO. introduced a new vessel cleaning equipment, *Can Clean*, able to clean any cylindrical vessel, as well as showing their range of *Vibrofiltro* filters.

WINKWORTH MACHINERY LTD. exhibited a new 1.5 pint laboratory heavy masticator.

Instruments

ELCOMETER INSTRUMENTS LTD. featured a wide range of instruments used for the application and testing of coatings. FERRANTI LTD. exhibited their well-known coaxial cylinder viscometer with one or two design modifications. A completely new particle size analyser, fully automatic, was shown by JOYCE LOEBL LTD. Leading colour measuring companies are now merged in KOLLMORGEN (UK) LTD. who demonstrated the *Trilac* spectrophotometer, a recording instrument of French design with many interesting features, including variable illumination and viewing geometry.

RUDOLPH MEYER'S INC. demonstrated the comprehensive range of ink properties which can be evaluated on the *Tack-O-Scope* and *IGT* printability tester. MICROSCAL LTD. featured a photosedimentometer for rapid determination of particle size distribution and a number of developments of the flow microcalorimeter designed for measuring heats of absorption of powders and heat of mixing liquids. PRUFBAU exhibited the *Prufbau Printer*, a machine designed to simulate wet on wet printing and having built-in temperature control, pressure and speed adjustments, adjustable printing intervals between units and an automatic roller washing device. REDIFON-ASTRODATA LTD. displayed the production version of the *Redi-Color* analogue computer for colour match prediction. The latest versions of the RESEARCH EQUIPMENT (LONDON) LTD. range of testing apparatus were demonstrated. RK CHEMICAL CO. LTD. exhibited a range of *K hand coaters* capable of the unusual range of 4 microns to 500 microns and the *K gravure printer* claimed to have the advantage over existing testers of maintaining doctor blade settings consistently over a number of tests and allowing fast and easy cleaning. SHEEN INSTRUMENTS (SALES) LTD. featured a range of instruments of particular interest for the application and testing of surface coating films, resins and paints.

Commendation Award

Photo by courtesy of Paint, Oil and Colour Journal

Mr L. J. Brooke (left) a Vice-President of the Association, presents Mr W. J. McWaters with the Commendation Award scroll, watched by Mr D. S. Newton (Chairman, Bristol Section)

As noted in the report of the January Council Meeting published in the April issue of the *Journal*, Council has approved the institution of a Commendation Award for outstanding and long service to the Association, particularly at the Section level.

It was decided that the first recipient should be Mr W. J. McWaters, of the Bristol Section, and the presentation of a decorated scroll commemorating the award was made at the Bristol Section Dinner Dance on Thursday 20 February, by Mr L. J. Brooke, a Vice-President of the Association, in the unavoidable absence of the President.

Mr McWaters was given the Award in acknowledgement of his service as Hon. Treasurer of the Bristol Section from 1948 to 1969, and his assistance in the formation of the Irish Branch, now the Irish Section.

Mr D. S. Newton, Chairman of the Bristol Section, had earlier welcomed members and guests to the dinner, including Mr K. Chitty, Chairman, Thames Valley, Mr R. N. Wheeler, Chairman, London, and Mr D. Woodfield, President, Birmingham Paint, Varnish and Lacquer Club, with their ladies. Mr Woodfield replied on behalf of the guests.

Oil and Colour Chemists' Association

The Council of the Association
record its gratitude to

William James McWaters

and has authorised the presentation of this

Commendation Award

in recognition of his outstanding service to the Bristol Section of the Association in his capacity as Honorary Treasurer of that Section from 1948 to 1960, and his assistance in the formation of the Irish Branch of the Section in 1961 which, since that time, has itself achieved Section status.

P. Shenton
Section Chairman

President

R. H. Hamblin
Director & Secretary

I. C. R. Bews
Honorary Secretary

28th January 1969

Meeting of Council

A meeting of Council, at which 16 members were present, was held on Tuesday, 25 February 1969 at Wax Chandlers' Hall, Gresham Street, London, EC2, with the President, Mr F. Sowerbutts, in the Chair.

Members were saddened to learn of the deaths of Mr A. H. Whitaker, an Honorary member of the Association, and Mr J. A. Frome Wilkinson, President of the Association 1932-34. As a mark of respect the Council stood in silence for a few moments. Obituaries have already appeared in the April issue of the *Journal.*

The Report of the Finance Committee for inclusion in the Annual Report of Council for 1968 was accepted, and Council agreed nominations for office as Hon. Officers to be placed before the Association's Annual General Meeting and for inclusion on the Agenda for that meeting which will be held in Eastbourne on 20 June.

It was reported that the Presidents of FATIPEC and the Scandinavian Federation had accepted invitations to attend the Association's Conference in Eastbourne (17-21 June) and it was hoped that the President of the Federation of Societies for Paint Technology would also be present.

Prior to the meeting members of Council had received copies of the Provisional Income and Expenditure Account and Balance Sheet for the year ended 31 December 1968, which were adopted. Copies of the Final Accounts will be circulated to members in due course.

It was reported that 46 members had volunteered to help Mr J. A. L. Hawkey with the compilation of the report on stands at 21 OCCA, the Association's Technical Exhibition.

Now that the revised editions of Parts I and II of the Paint Technology Manuals are available, it was reported that consideration was being given to the rewriting of Part III. The complete draft of Part VII (Works Practice) had been submitted to the Hon. Editor, but no date for publication could be given.

Members appointed to represent the Association on BSI Committees were as follows:

Dr B. S. Gidvani on Committee PVC/4 & PVC/4/1—Lac.

Mr J. L. Orpwood on Committee OC/20/4/12—Chemistry and Chemical Technology.

Dr J. B. Ley on Committee on Organic Finishes for Aluminium Windows.

In addition, Council appointed Mr R. M. W. W. Wilson to represent the Association on the East Ham Technical College Advisory Committee.

It was reported that the Jordan Award Committee would meet in April to consider the applications received.

Reports on Section activities were received and it was noted that some Sections were planning Symposia, details of which will appear in the Journal in due course.

In addition to the two Sections, Hull and Newcastle, who were already undertaking research projects, it was reported that the Manchester Section was also making arrangements for a project.

Reports from the two working Parties set up under the Forward Thinking Project were received. The first report with recommendations from the Working Party on Education, Training and Qualifications was noted, referred back to the Working Party for further details and to the Section Committees for discussion before the meeting of Council on 30 April, when the recommendations were to be discussed fully.

News of Members

Mr F. W. Davies, an Ordinary Member attached to the Manchester Section, has recently been appointed to the Board of Directors of Cornbrook Resin Company Limited. Mr Davies was previously General Sales Manager.

Mr K. D. Rutter, an Associate Member attached to the London Section, has taken over as Managing Director of Bakelite Xylonite Limited as from 1 April. Mr Rutter was previously Managing Director of Union Carbide (UK) Ltd.

Metrication and the printing ink industry

The Council of the Society of British Printing Ink Manufacturers has recently unanimously recommended its members to be prepared to change over to the metric system on an industry basis on or about 1 January 1971, thus (a) coinciding with the declared intention of the Printing, Paper and Packaging Film Industries to effect the change-over by the end of 1970, and (b) anticipating the official change to decimal currency on 15 February 1971.

It is hoped that this official announcement by the Society will clarify the position of the printing ink industry, and serve to minimise requests from individual printers to their ink makers to supply inks in metric units of weight before the recommended date.

SCI Lancaster Symposium

The Society of Chemical Industry is to hold a symposium entitled "New horizons for chemistry and industry in the 1990s" at the University of Lancaster from 7 to 11 July 1969.

A full programme of lectures, works visits and social events has been arranged.

Federation of Societies for Paint Technology

Availability of Unit 10 in the "Federation Series on Coatings Technology," entitled "Black and metallic pigments" has recently been announced. Copies of the 56-page booklet are obtainable from the FSPT at 50c per copy.

It has also been announced that the Roon Foundation Awards will be continued, and will be awarded for the best technical papers offered for presentation at the 1969 Annual Meeting of the FSPT. Last date for receipt of papers is 1 July 1969, and seven copies should be submitted to Dr M. J. McDowell, c/o the du Pont Co., 3500 Grays Ferry Avenue, Philadelphia, Pa. 19146, USA. A total of $1,750 is available for the awards.

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication, and in South Africa and the Commonwealth up to the end of the second month.

Friday 2 May

West Riding Section. Luncheon Lecture, to be held at the Astoria Ballroom and Restaurant, Rounhey Road, Leeds, at 1.0 p.m. A talk on "The Role of the Trade Journal in Surface Coating Industry," will be given by Mr D. Eddowes, Editor, Paint Oil & Colour, Journal.

Tuesday 6 May

West Riding Section. Works visit to Messrs. Wood Brothers Glass Co. Ltd., Borough Flint Glass Works, Barnsley, Yorkshire, commencing 2.30 p.m.

Friday 9 May

West Riding Section. North of England OCCA Golf Trophy, to be played at the Pannal Course, Harrogate, commencing 1.30 p.m.

Friday 16 May

London Section—Southern Branch: Social Evening, with Hovercraft trip to Isle of Wight.

Tuesday 17 June-Saturday 21 June

Association Biennial Conference, "Film Formation and Curing," to be held at The Grand Hotel, Eastbourne.

Friday 20 June

Annual General Meeting, to be held at the Grand Hotel, Eastbourne, at 2.15 p.m.

Saturday 21 June

Newcastle Section. Annual Golf Match for the British Titan Cup, to be held at Brancepeth, Co. Durham.

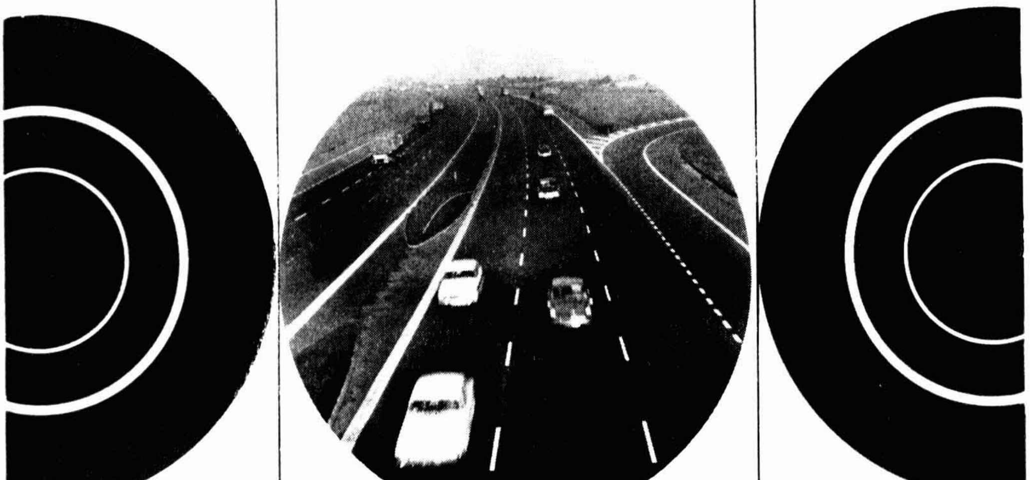
EGUSSA – Colour Blacks for lacquers and printing inks

	Depth of colour N. I.	Tinting strength	Oil absorption g/100 g	
gent Super	58	0,75	840	Readily dispersing and of the deepest blackness, a top quality carbon black for top quality lacquers.
V 2 V *	63	0,78	700	Very deep black standard pigment for high-quality lacquers, disperse readily
V 200 *	63	0,73	540	For deep black thermosetting acrylics.
170	71	0,98	650	Medium black giving high degree of opacity.
ecial Black 5 *	75	0,83	430	For black lacquers of all kinds, plastics, printing inks
ecial Black 4 *	80	0,86	300	Medium black, disperses readily, high opacity, for letterpress, offset and gravure printing inks, highquality industrial lacquers.
ss L-T	81	0,66	360	For lacquers, carbon papers, plastics, typewriter ribbons
ss L-TD	81	0,66	360	
ecial Black 4 A	80	0,86	230	Black pigment for high-quality modern illustration inks, carbon papers, ink ribbons and duplicating inks
1000 V	83	0,95	400	Pigment for black industrial lacquers, and grey lacquers with brown tint. Standard quality for rotary, offset and gravure inks
Carbon Black 140 V*	84	0,91	360	For rotary inks, carbon papers
Printex 400	84	1,01	330	For printing inks, typewriter ribbons, carbon paper
Carbon Black 30 *	90	0,91	400	For rotary inks and cement mixes.
Carbon Black 300	90	1,00	360	For rotary inks and gravure printing inks with good flow, for cheaper letterpress and offset inks, for carbon papers
Carbon Black A *	94	0,73	300	For multi-colour shading and newspaper inks
Carbon Black G *	98	0,64	250	Blue-tinted, for multi-colour shading and newspaper inks
Lamp Black 700	93	0,66	400	Tinting pigment for the lacquer industry, as for printing inks with good flow characteristics especially gravure inks
Lamp Black 101	102	0,21	280	For tinting with blue shade, in combination with Printex or Printex 140 for newspaper inks

lly and beads

How many grooves in this record? Of course – only one. The groove makes the music. So that it can do this, the record is pigmented black with about .5 per cent carbon black. This is done with a superfine-particle gas black. The mean particle size is 10 to 20 thousandths of a micron. About a trillion particles to one gramme of carbon black! Extreme fineness, deepest black, high degree of fastness – these three points make carbon black the most popular of black pigments. DEGUSSA carbon blacks are also popular for pigmenting paints, printing inks, plastics, synthetic fibres, papers and building materials. Sales concessionaire in the U. K.: Bush Beach & Segner Bayley Ltd.,
175, Tottenham Court Road, London W. 1
Tel. 01-580 8041 (8 lines)

DEGUSSA



PEINTURES

PIGMENTS · VERNIS

Founded in 1923

Published under the patronage of the French National Federation of Paint, Varnish and Printing Inks manufacturers.

This journal is of a scientific, technical, economic and professional character and contains, apart from the editorial, columns on Technology, Rheology, Technical Information, Industrial Research News, Documentation, Economy, Information, Apparatus, New Products and Processes.

It is, therefore, intended not only for scientists and technicians in research laboratories and enterprises in the field, but also for suppliers of raw materials and manufacturers of materials.

Cost of a yearly subscription:

France: 60 Francs. Abroad: 72 Francs

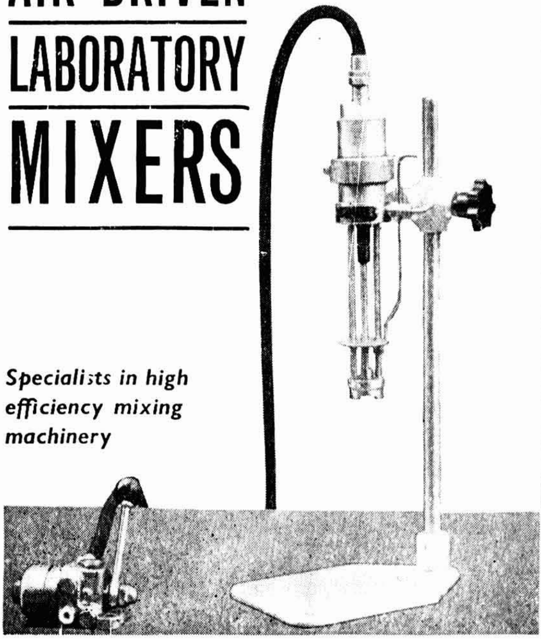
Specimen copies available on request directly from the Editor:

SOPRODOC: Commercial Department,
80, Route de St-Cloud, 92-RUEIL-MALMAISON (France) Tel: 967-77-95

Exclusive Representatives for Great Britain:

BRITISH OVERSEAS MEDIA BUREAU REPRESENTATIONS LTD.,
16-17 Bride Lane, Fleet Street, London EC4. Tel: 583-0581

AIR DRIVEN LABORATORY MIXERS



Specialists in high efficiency mixing machinery

for hazardous conditions

Capable of infinitely variable speeds up to 10,000 r.p.m.

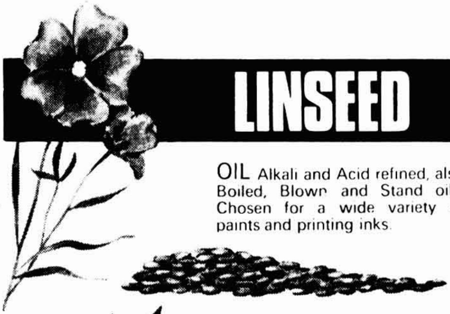
The machine is capable of emulsifying, homogenising, dispersing and preparing Heavy Pastes. The adjustable deflector prevents admission of air and reduces the vortex to a minimum.

Brochures of this and other types of Mixers and Agitating Gears available from:

Joshua Greaves & Sons Ltd.-Dept JOCCA
Ramsbottom, Bury, Lancashire
Telephone: RAMSBOTTOM 3159
Telegrams: GREAVES Ramsbottom


SUPERB
GREAT NE
OFFE
save
NEW
VALUE

Vegetable Oils raised from seed



LINSEED

OIL Alkali and Acid refined, also Boiled, Blown and Stand oils. Chosen for a wide variety of paints and printing inks.

SOYA BEAN

OIL A semi-drying oil, Alkali refined and Blown, whose properties make it particularly useful in the manufacture of alkyd resins for paints.

SUNFLOWER

SEED OIL Alkali refined with semi-drying properties, particularly useful in paints and artists colours. A useful addition to the vegetable oil range.

All the oils described above are obtainable in light steel drums or in bulk. Special grades can be produced if required, further details and specifications are available from —

Samuel Banner
& CO. LTD.

Liverpool: 34 Castle Street 051—236 0223
London: 10 Newton Road, E.15 01—534 4321
Glasgow: 289 Castle Street, C.4 041—BEL 0723

DEDICATED WORKERS

These minute larvae of the lac insect will devote their six-month life cycle to playing their part in the production of lac—the vital natural base material for **SWANLAC BLEACHED LACS** (transparent, waxy or modified) **SHELLACS LAC ESTERS & HYDROLYSED LAC**

You will find us equally dedicated to the task of meeting your lac requirements, likewise those for natural **VARNISH RESINS, WAXES & WATER GUMS**

·SWANLAC·

A.F. SUTER & CO. LTD.
Cereal House
58 Mark Lane
London E.C.3
Tel: 01-709-9449
Telegrams
Suteresin
London E.C.3

Agents for Established 1906
ANGELO BROTHERS SHELLACS

A few more foam truths

about effective, efficient Nopco paint defoamers

We've already reminded you of the problems of foam during high speed mixing. The wastage it causes. The adverse effects it has on the quality of the final product.

And we've told you about three of Nopco's top foam killers:

● Nopco* NDW, probably the best all round defoamer in the world today.

● Nopco* NXZ, specially for synthetic latex emulsions and cleared by the FDA for adhesives used in food packaging; and Nopco* PD-1, the powder defoamer that blends easily with all dry mix formulation compounds.

Now here are some more big guns in the Nopco anti-foam arsenal:

● Nopco* 1407 – an efficient, low cost paste anti-foam, compatible with most latex systems. Two to five pounds per 100 gallons of paint does the job. And it's FDA approved.

Nopco* DD-72 – A 99% active liquid defoamer requiring low levels of addition for optimum effectiveness.

● Nopco* DNH-1 – provides excellent anti- and defoaming properties to all major latex paint systems.

● Nopco* 1419-A – An economical, 100% active liquid defoamer, light in colour, efficient for most systems, FDA approved.

● Nopco* 8034 – A defoamer for low particle size emulsions. 100% active, liquid, easy to use. Very good additive for all PVA systems.

● (denotes products recommended by one or another of the leading latex manufacturers or suppliers).

To help you choose the right defoamer for the job, the Nopco Technical Advisory Service is always available for consultation. For full information on this service plus comprehensive literature on the new, extended range of Nopco chemicals for the paint industry, please contact:

NOPCO HESS LIMITED

NOPCO
CHEMICALS FOR QUALITY CONTROL

Department No. A11
147 Kirkstall Road, LEEDS 3.
Telephone: Leeds 38837.
Cables: Nopco Leeds.

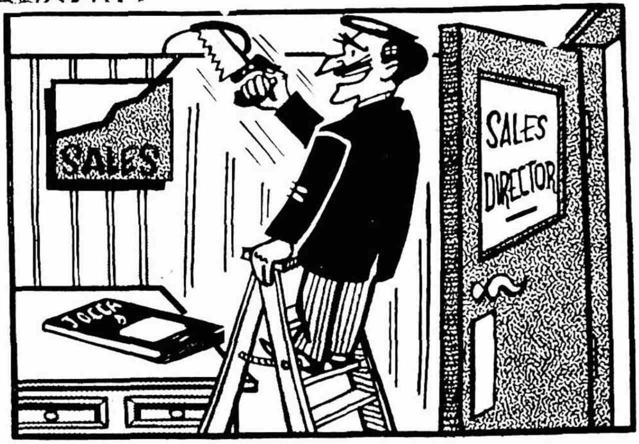
* *Registered Trade Mark*

They whispered that he hadn't a clue . . .

. . . and the Sales Manager felt a dismal failure. He knew that the raw materials marketed by his company for the paint, printing ink and allied industries were first class, but somehow he just could not make any headway.

It had even affected his Saturday round of golf, and he had become the butt of his caddie's wit. And then, one day at an O.C.C.A. Technical Exhibition† he met an old colleague, Doctor Y., now the Technical Director of a paint company, who immediately expressed surprise that the Sales Manager's company did not advertise in JOCCA*

"Take it from me," said the worthy Doctor, "the first thing I'd recall in your position is that JOCCA* has an unrivalled world-wide circulation among the technical personnel, who create the demand for raw materials, plant and equipment. That's why so many companies take advertising space in its pages. And, another thing, I hear that the print order's just been increased again . . ."



Nowadays, of course, the newly promoted Sales Director has a purposeful, confident look, and the current number of this Journal is always on his desk.

For full details of advertising in this important medium write to :

Journal of the Oil & Colour Chemists' Association*
Wax Chandlers' Hall, Gresham Street, London E.C.2.

---

†*The Twenty-first took place* 24-28 *March* 1969

CLASSIFIED ADVERTISEMENTS

SITUATIONS VACANT

SURFACE COATING RESINS

TECHNICAL SALES REPRESENTATIVE FOR THE SOUTH OF ENGLAND

B I P Chemicals Ltd., Oldbury, have a vacancy for a Senior Technical Sales Representative to promote the sale of Surface Coating Resins in the South of England. Occasional overseas visits may also occur. Applicants should have a sound technical knowledge of the paint industry and in particular, the field of industrial stoving finishes. Training will be arranged at the Company's Laboratories at Oldbury, Birmingham, after which the successful applicant will be based at the Company's Sales Office in London. Preliminary interviews will be arranged in London. The Company offers excellent conditions of employment including a contributory Pension and Life Assurance Scheme. A Company car will be provided. Application should be made in writing, giving full details of age, experience and other relevant information, to the

Personnel Manager,
B I P Chemicals Ltd., Popes Lane,
Oldbury, P.O. Box 6, Warley, Worcs.

BIP
A TURNER & NEWALL COMPANY
TN

PRINTING INK TECHNOLOGIST

Western Ink Co. Ltd. require a Liquid Inks Chemist aged 22 to 26 to join an expanding team.

We are specialists in the manufacture of flexographic and gravure inks, are currently expanding considerably and consequently seek additional technical talent in this field. Thus, if you are in our required age-range, have qualifications in ink technology, experience in liquid inks and can offer vision, energy and that professional self-discipline which customers appreciate, we in turn will make you a worthwhile offer. This could include renting a Company house or advantageous mortgage facilities.

Our works are situated in Somerset countryside only 11 miles from the centres of Bristol and Bath.

Please write, giving full details of your career to date to **The General Manager, Western Ink Co. Ltd., Paulton, Bristol BS18 5LQ**, who guarantees absolute confidence regarding your application.

SITUATIONS VACANT

Opportunities in AUSTRALIA

F. T. WIMBLE & CO. LIMITED
Printing Inks Division

The Company
is a major supplier of inks in all States of Australia and in New Zealand. As a result of dynamic marketing oriented policies, the Company is now seeking to expand its technical division to meet the demands of the printing industry.

Central Research Laboratory Manager—Sydney
This is a new key position within the Company structure and promises to be most interesting and challenging.

We need a graduate chemist with a recognised degree or diploma in chemistry with or without an ARIC or RACI. Whilst it is preferable that applicants have experience in the ink industry, it is by no means a prerequisite. Experience in allied fields such as paints, lacquers or adhesives will be sufficient.

Top salary and conditions assured.

Chief Chemist—Melbourne
The Company is looking for one of the best men in the industry. He is probably now near to the top of the technical function in a large organisation and should desirably have a background in the formulation of all types of inks. A sound record in leadership of technical staff is essential. A Company Car will be provided and the salary level will be determined by the figure it is necessary to attract a top man.

Laboratory Technicians
Positions are available in all States but principally in NSW and Victoria. Experienced offset, Letterpress, Gravure, Flexo or Silkscreen ink technicians are required. Your practical training could be in any one of the following laboratories—raw material, testing, evaluation of raw materials, formulation, colour matching, technical service, analysis, quality control, development or research.

Excellent opportunities for personal advancement

Field Technicians
for the Company's Customer Service Division in both NSW and Victoria. Technically qualified and/or experienced executives with specific knowledge of the printing industry.

This job offers prospects of advancement into Sales Marketing areas.

Please write in absolute confidence quoting position being applied for, to T. S. Goldfinch, Company Secretary, F. T. Wimble & Co. Ltd., 11 South Street, Rydalmere. NSW 2116. Australia.

We will not disclose any information on your interest in any one of the above positions without your personal permission.

Applications
Please set out full details of past experience, present position together with relevant references.

The Company will arrange passages to Australia and accommodation on arrival.

SITUATIONS VACANT

PAINT TECHNOLOGIST

(OR ASSISTANT CHEMIST)

required by Bryce Weir Ltd., Watford, Herts, paint manufacturers, for development work on industrial paints. The Company is a subsidiary of Albright & Wilson Ltd. Preferred applicants will have considerable experience in paints though they may not possess academic qualifications. Alternatively a young graduate without much experience would be considered. Assistance may be given with house removal.

Apply in first instance to:

Staff Officer,
Albright & Wilson Ltd.,
1 Knightsbridge Green,
London, S.W.1.
(*Ref. 929*)

SITUATIONS WANTED

General Manager (middle forties) of Pigment Division in large overseas paint company manufacturing inorganic and organic pigments, litharge, red and white-lead and electrolytic cuprous oxide, returning to England in May, seeks technical or sales position in comparable fields or in industrial chemicals. Over 20 years' experience in England and overseas. Fluent Portuguese and good Spanish. London or Home Counties preferred. Box No. 305.

CONSULTANTS

ACCELERATED WEATHERING
&
ENVIRONMENTAL TESTING
40 years' Experience. Latest UK Equipment

W. H. & E. Moss,
16 Green Park,
Prestwood, Bucks.

SITUATIONS VACANT

SITUATIONS VACANT

TECHNICAL MANAGER

Redcliffe Inks Limited, which is a member of the Dickinson Robinson Group, an international packaging and stationery organisation, manufactures all types of printing inks for the packaging industry. This progressive Company is located near pleasant countryside in South Gloucestershire.

The Technical Manager will be responsible to the Managing Director for organising a technical team engaged in maintaining and developing a product range to meet a wide variety of inks aimed at the packaging market.

Applicants who should be in the age group 35/45 must possess a University degree or equivalent qualification and have had some experience in a management position in the printing ink or an allied industry. The Company forms part of a large Group where there are opportunities of further advancement for men of outstanding ability.

Salary and salary progression are attractive and the Company operates pension and life assurance schemes.

Application quoting ref: HX to: The Personnel Manager,

E S & A Robinson (Holdings) Ltd.,
Bristol 1.
a DRG company

BOOKS

DR. W. M. MORGANS, F.R.I.C.

Outlines of

PAINT TECHNOLOGY

Pigments, Solvents, Media, Pigmented Coatings, Applications, Testing

Industrialist, consultant, and lecturer at the Borough Polytechnic, Dr Morgans is the ideal technical exponent in the light of the latest advances. His book, written to replace Heaton's classic, will be well-thumbed wherever paint is made or used.

426 pp, many illus., references, bibliography. £4 4s (carr. 4s)

Full prospectus from **GRIFFIN** *42 Drury Lane, W.C.2*

Oil and Colour Chemists' Association

President : F. SOWERBUTTS, B.SC.TECH.

The Oil and Colour Chemists' Association was formed in 1918, to cover paint, printing inks, pigments, varnishes, drying and essential oils, resins, lacquers, soaps, linoleum and treated fabrics, and the plant, apparatus and raw materials useful in their manufacture. In 1924 it absorbed the Paint and Varnish Society. The stated purpose of the Association is to promote by discussion and scientific investigation the technology of the industries concerned with the above-mentioned products, and to afford members opportunity for the interchange of ideas. This is achieved by the regular holding of ordinary meetings at which papers are presented, and the organisation of annual technical exhibitions, biennial conferences, educational activities and practical co-operative experimental work. Details of these activities are given in the *Journal of the Oil and Colour Chemists' Association*, which is published monthly, and whose pages are open to receive communications and other pronouncements on scientific and technical matters affecting the members of the Association and the industries concerned. The Association's meetings also afford opportunities for members to meet informally and socially.

There are Sections of OCCA in Auckland, Bristol, Hull, Ireland, London, Manchester, the Midlands (with a Trent Valley Branch), Newcastle upon Tyne, Scotland (with an Eastern Branch), South Africa (with Branches in the Cape, Transvaal and Natal), Thames Valley, Wellington, and the West Riding, and these are responsible for the conduct of their own local affairs. There is also a General Overseas Section. There is also a close alliance between the Association, the Federation of Societies for Paint Technology in the United States, and the Fédération d'Associations des Techniciens de l'Industrie des Peintures, Vernis, Emaux et Encres d'Imprimerie de l'Europe Continentale (FATIPEC). The Association also maintains cordial relations with the Scandinavian Federation of Paint and Varnish Technicians (SLF).

The five Sections previously maintained by the Association in Australia formed (1.1.68) the Oil and Colour Chemists' Association Australia, having the same aims and activities as, and working in close liaison with, the parent body.

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Student Membership, which is intended primarily for students, is open without restriction to persons under the age of 21 and to those up to 25 who are following a course of technical study. The annual subscription in each case is five guineas, except for Student Members whose subscription is one guinea. An entrance fee of 10s. is payable by all members. Applications for membership are invited from suitably qualified persons who are engaged or otherwise interested in the industries noted above. Applications, which should be supported by two members of the Association (one of whom must be an Ordinary Member), should be forwarded to the Director & Secretary at the address given below. Application forms and full details of membership may be obtained from the offices of the Association.

PUBLICATIONS

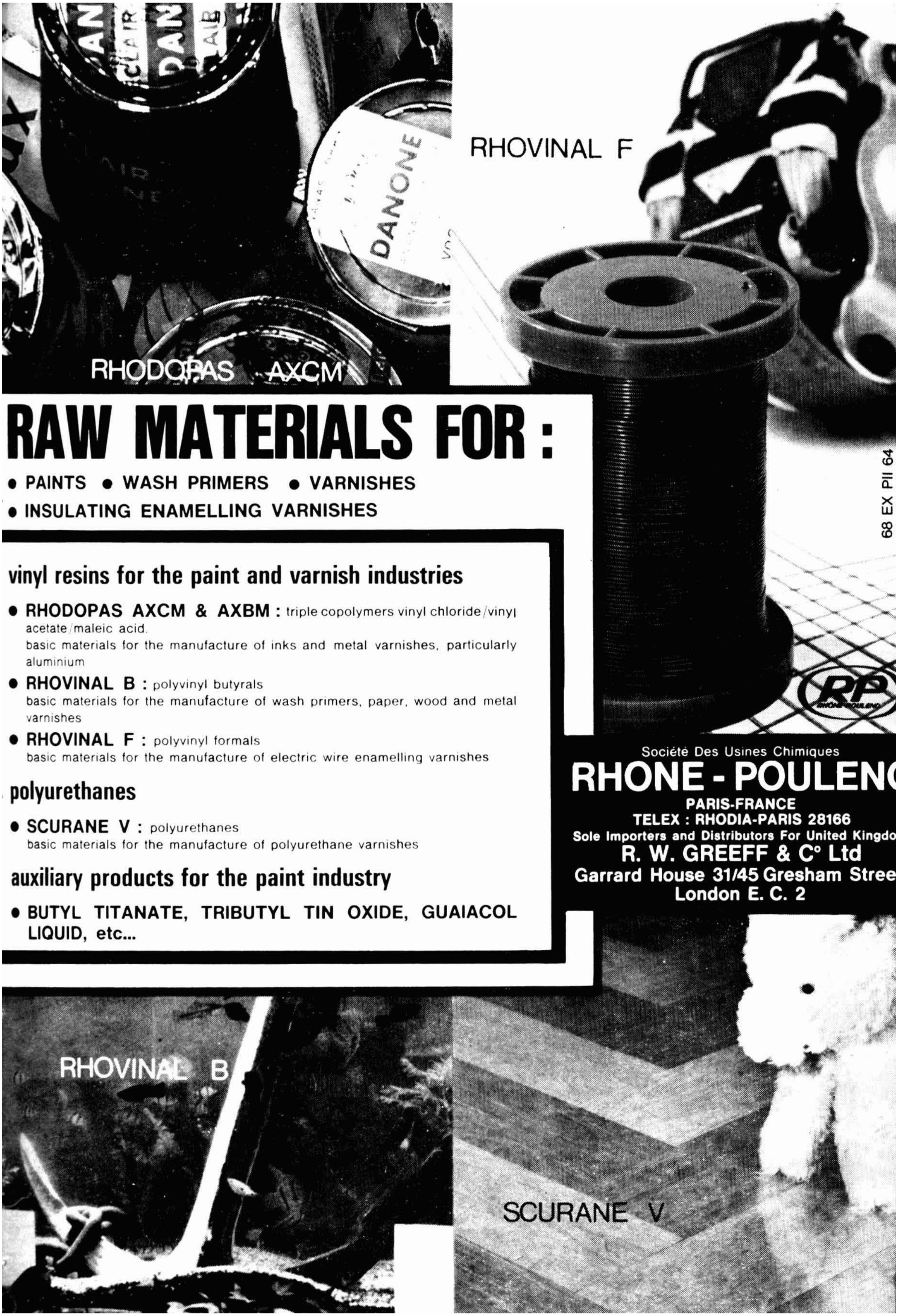
Journal of the Oil and Colour Chemists' Association. Published monthly. Subscription rate to non-members in UK and abroad, £7 10s. p.a. post free ; payable in advance.

An Introduction to Paint Technology (Second Edition with additional chapter). Pp. 187, illustrated, with index, £1 (including postage).

Paint Technology Manuals

Part 1 : " Non-convertible Coatings," Second Edition, Pp. 343, 36s.
Part 2 : " Solvents, Oils, Resins and Driers," Second Edition, Pp. 268, 36s.
Part 3 : " Convertible Coatings," Pp. 318, 35s.
Part 4 : " The Application of Surface Coatings," Pp. 345, 35s.
Part 5 : " The Testing of Paints," Pp. 196, 35s.
Part 6 : " Pigments, Dyestuffs and Lakes," Pp. 340, 35s.

Director & Secretary : R. H. Hamblin, M.A., F.C.I.S., F.C.C.S., Wax Chandlers' Hall,
Gresham Street, London, E.C.2.



BECKOSOL 1474 is a must for war paints. Paints that fight off fading, keep pale shades true to their colours and sustain white brilliantly under all conditions.
And Beckosol 1474 is a medium which imparts a smooth beautifully brushable flow, high build and a superbly hard high gloss finish.
In short an invaluable addition to all decorative enamels, undercoats, marine whites and topside paints.

SPECIFICATION (tentative)

Type		Pure drying alkyd
% Non-volatile		70.0
Volatile		White Spirit
Viscosity		$Z_1 - Z_2$
Colour		6-max.
Acid No. (soln)		9-max.
Specific gravity		0.96
White Spirit tolerance		20
Suggested thinner proportions.	White Spirit	100%
Type of Oil		Linoleic rich
% Fatty acid (base)		57.5
% Phthalic anhydride (base)		24.8
Resin and/or derivatives		Absent
Phenolic resin modifiers		Absent
Compatibility with:	Basic Pigments	Good
	Nitrocellulose	None
Miscibility with:	Drying Oils	Fair
	Varnishes	Fair

For further, full details, please enquire to the Sole Selling Agents

BECK, KOLLER & CO. (England) LTD., Speke, Liverpool 24.
Tel: HUNts Cross 1214
Associate Works: **Reichhold Chemicals Inc., Detroit, U.S.A.**

Sole Selling Agents
JAMES BEADEL & CO. LTD., Frodsham House, Edwards Lane, Liverpool 24
Tel: HUNts Cross 1395. Telex: 627297
London Office: **Hillgate House, 26 Old Bailey, E.C.4. Tel. & Grams: CITy 2405/7**
Members of the Reichhold Chemicals Ltd. Group of Companies