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21-OCCA PREVIEW

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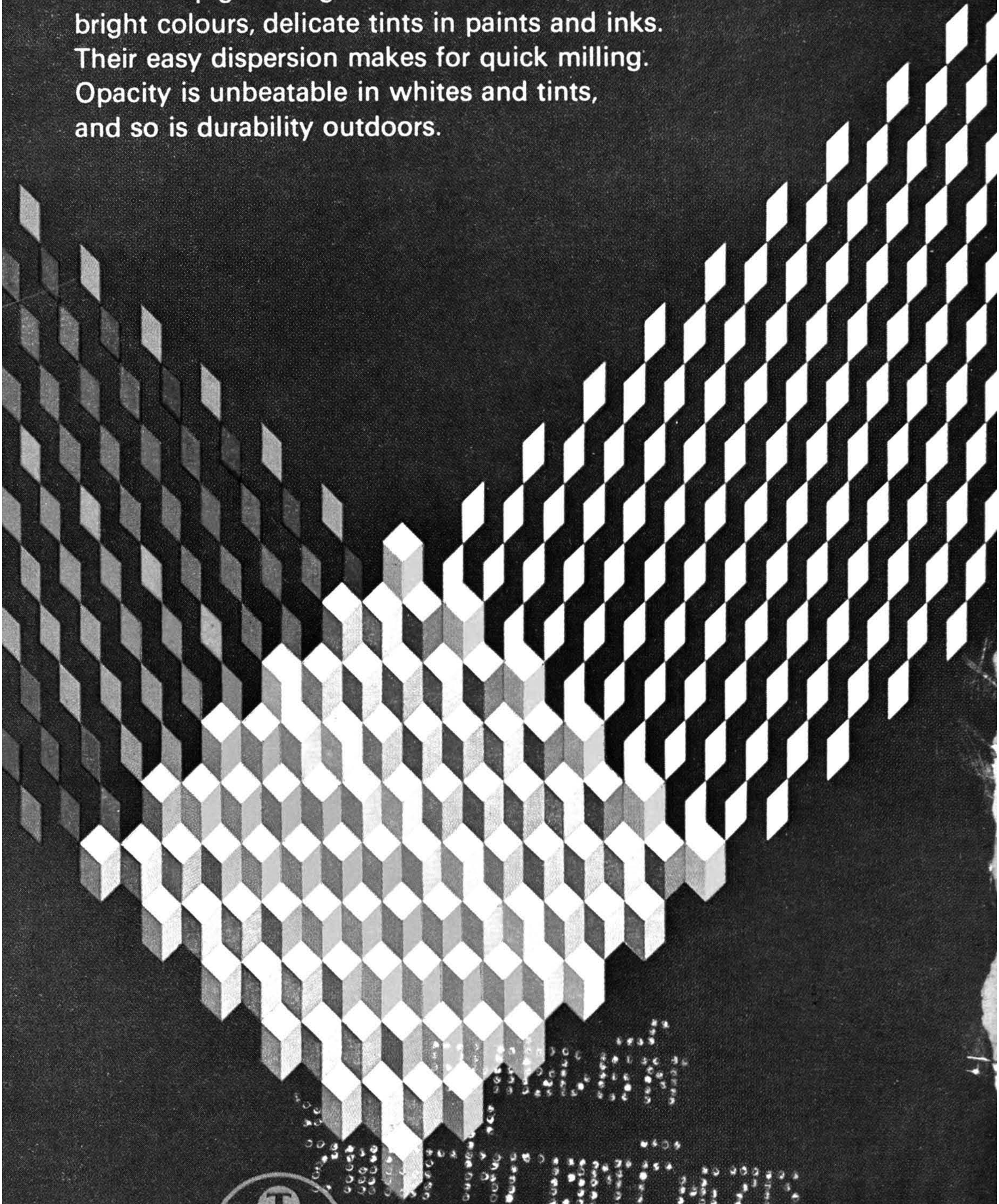

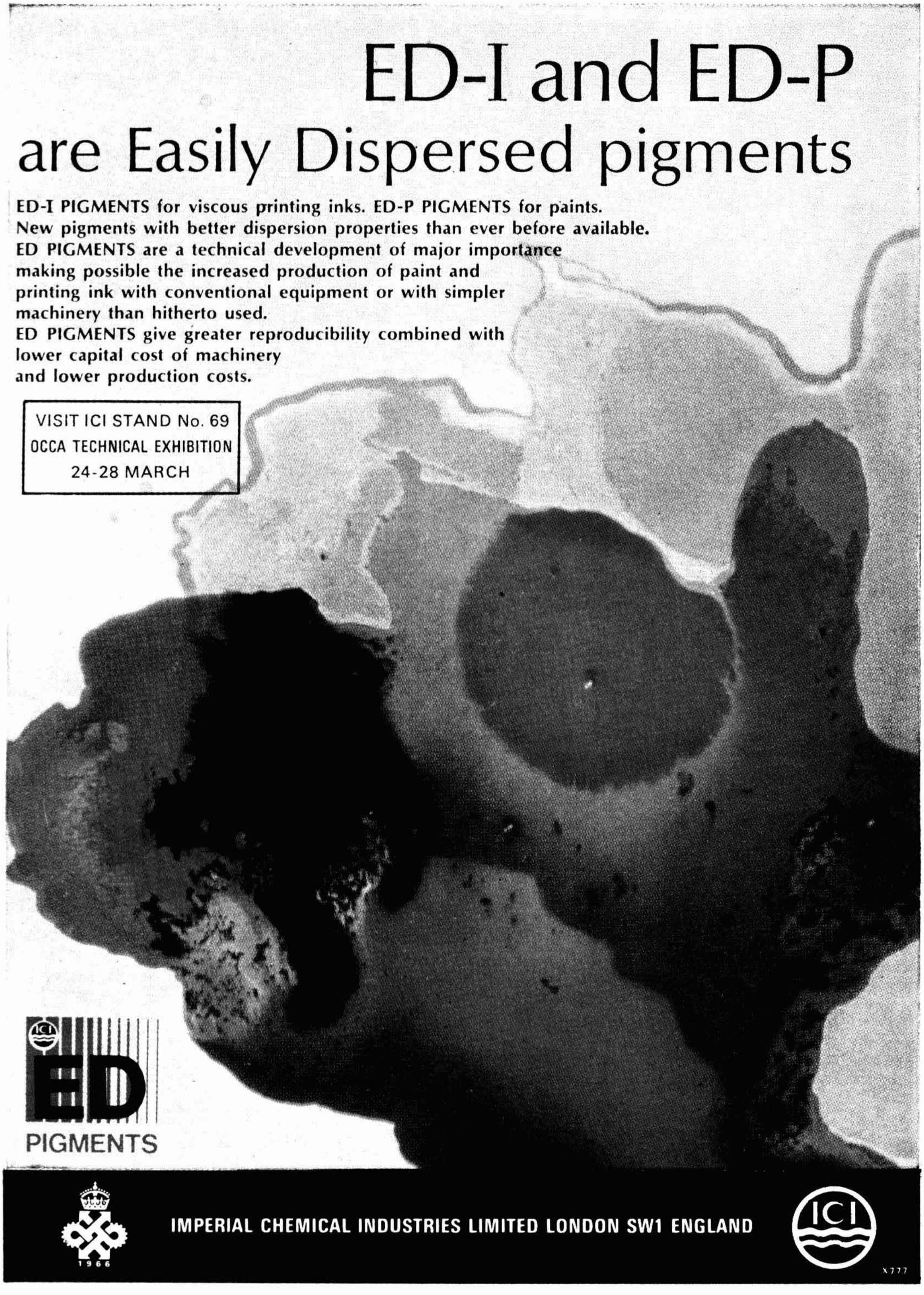

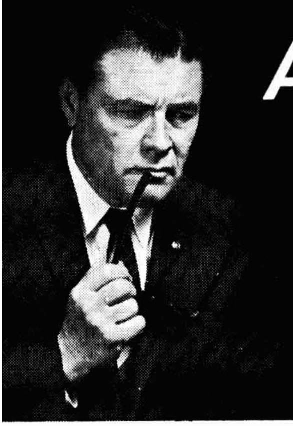

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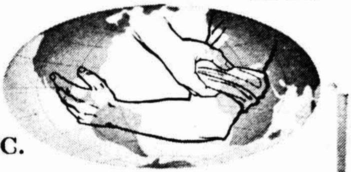

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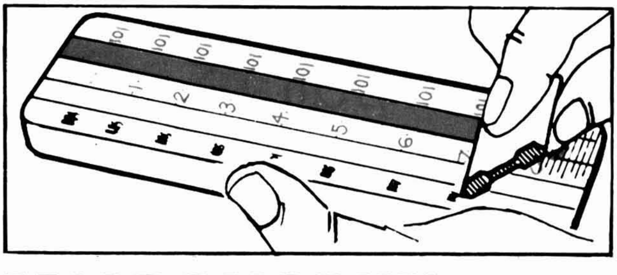
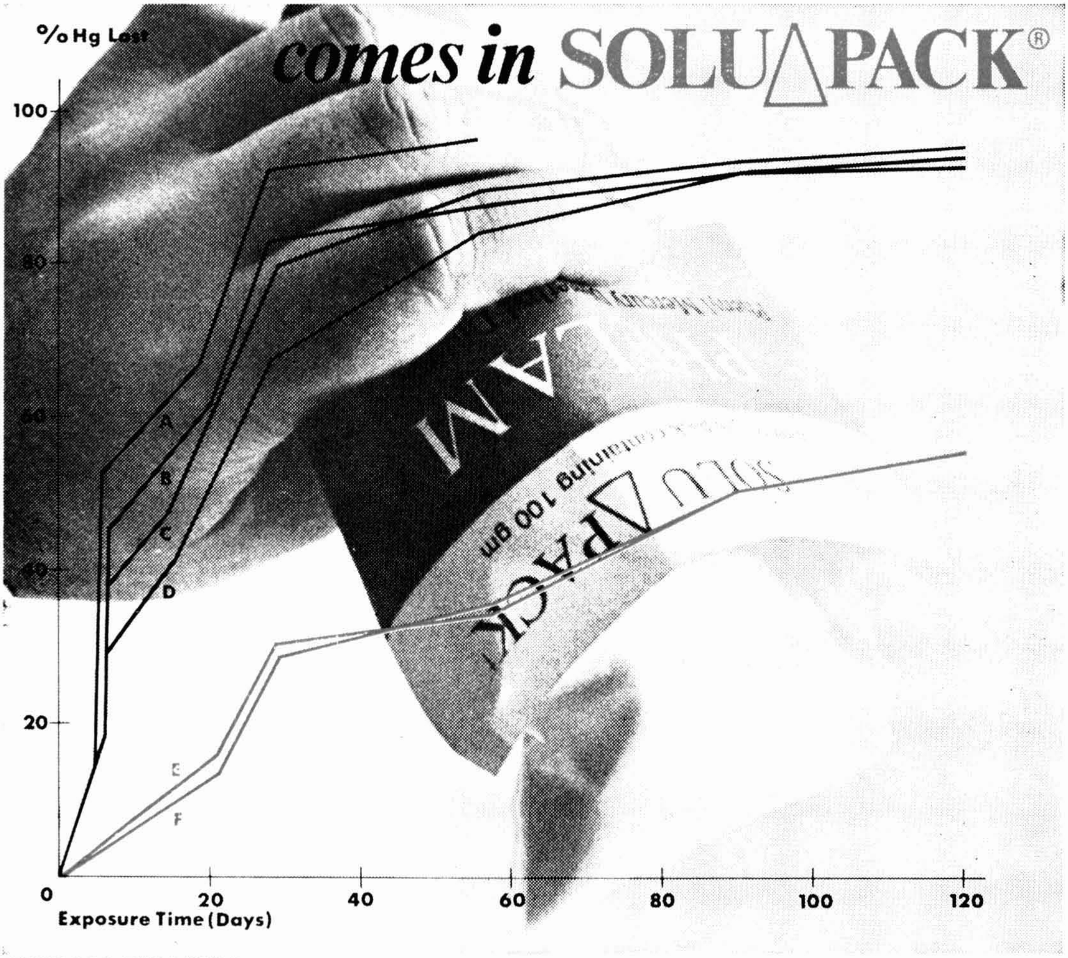
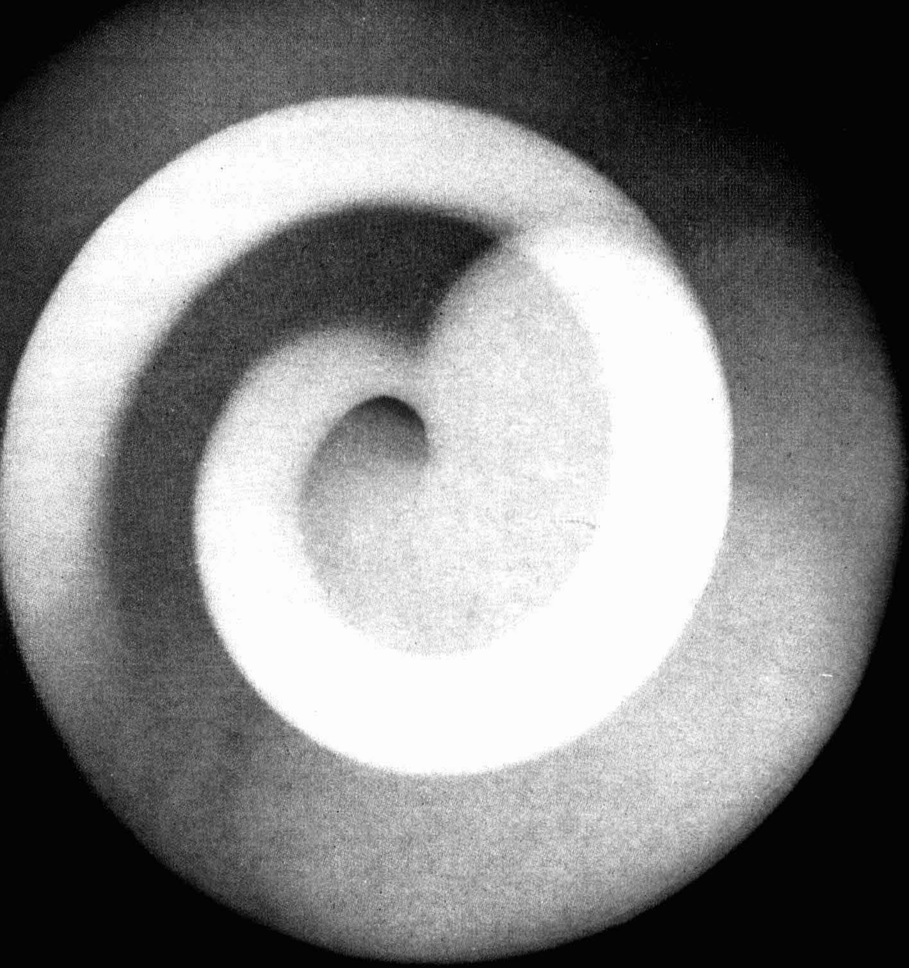
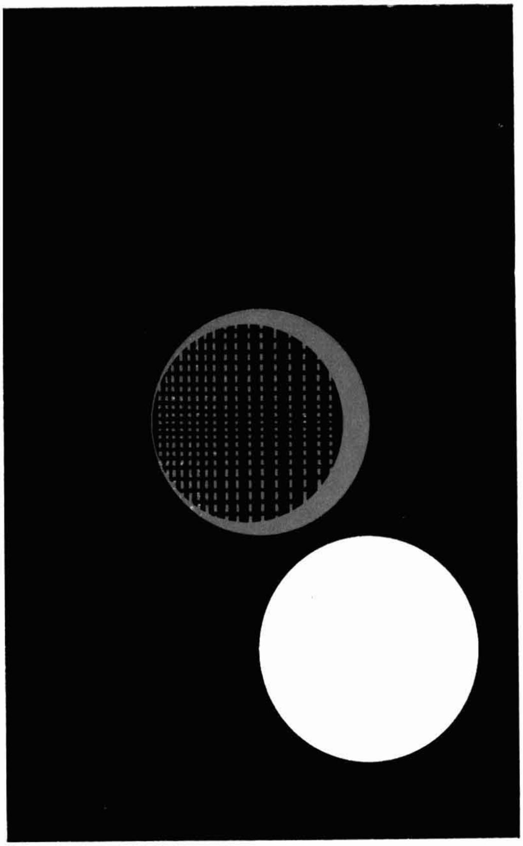


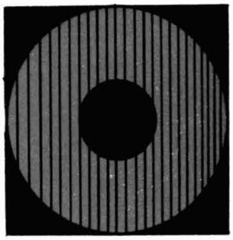


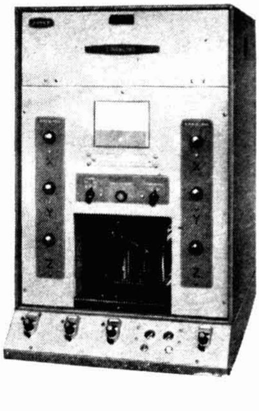
%Hg Lost
100
80
60
40
20
0
20
40
60
80
100
120
Exposure Time (Days)
A
B
C
D
E
F
PHELAM
SOLU△PACK
containing 100 gm




VP





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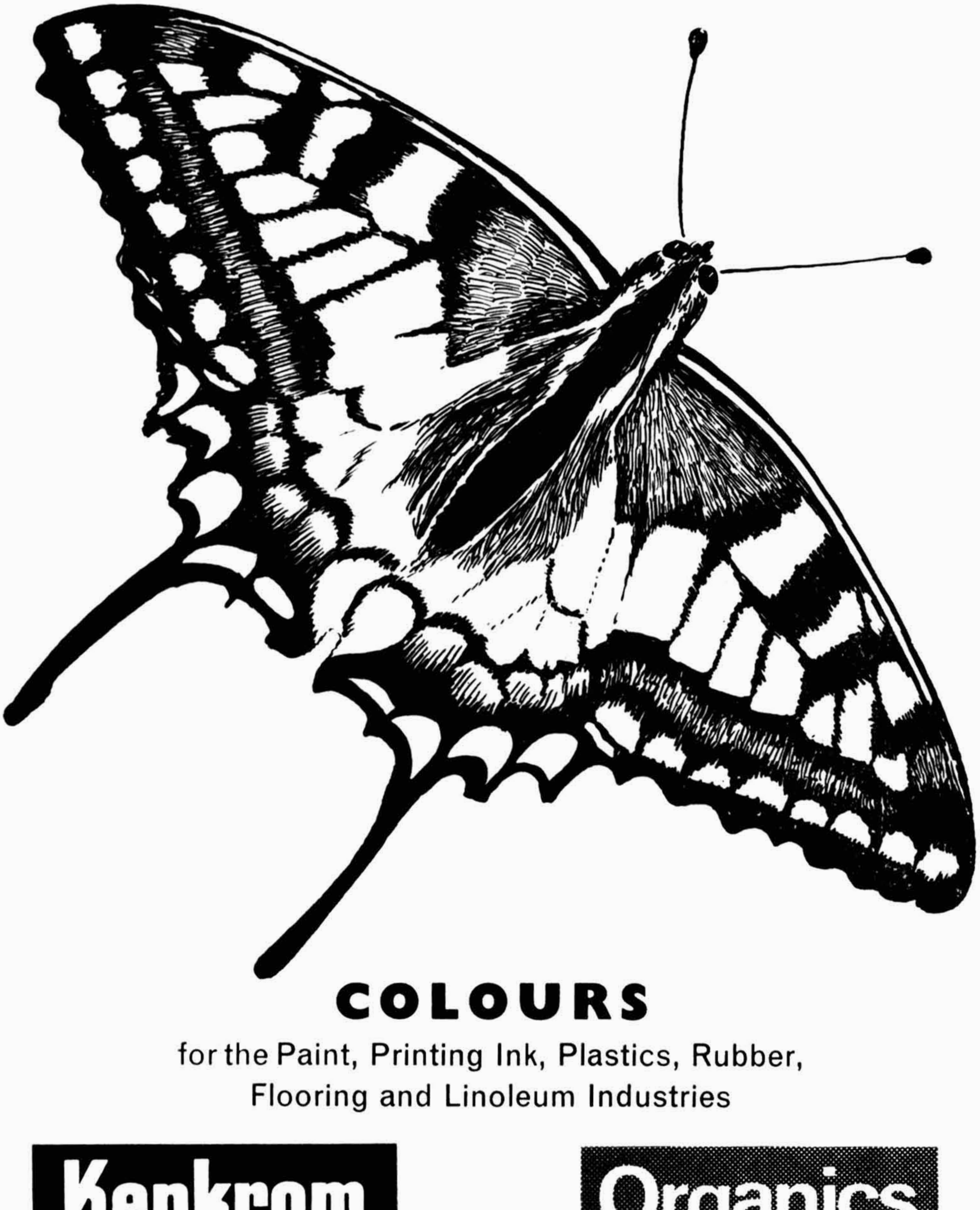

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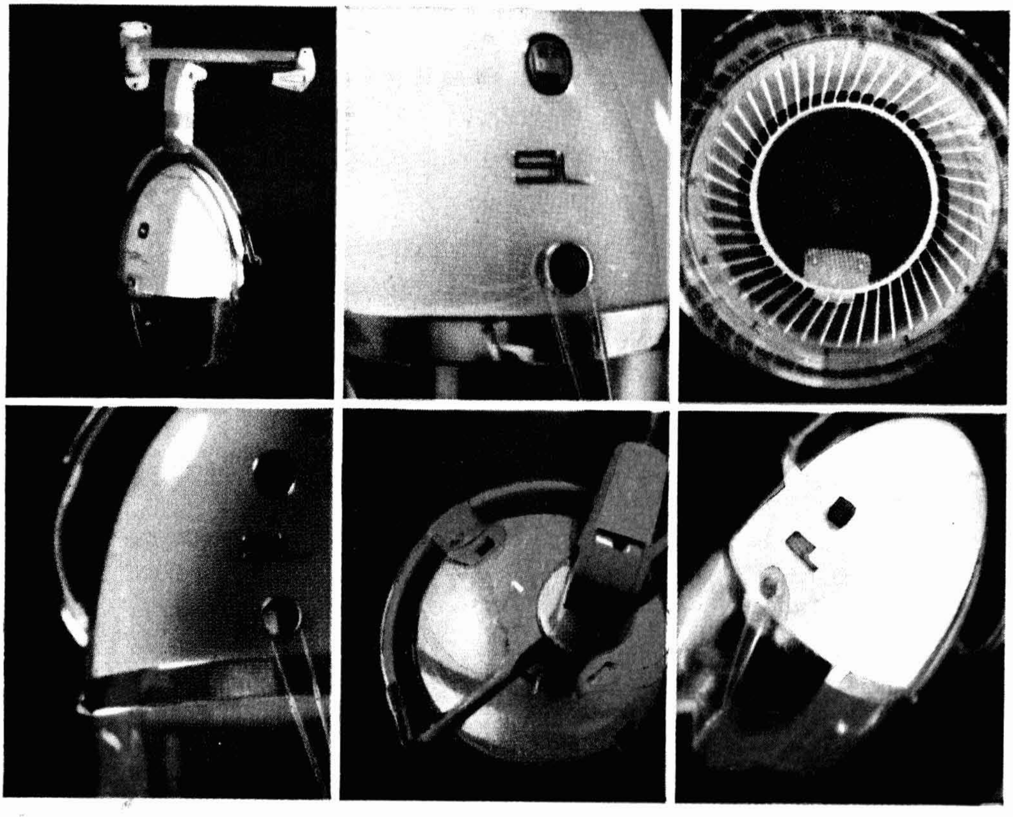

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Contents **Vol. 52 No. 3** **March 1969**

Transactions and communications

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Transactions and Communications

Formulation of fungus-resistant paints. IV: Addition of tetramethyl thiuram disulphide

By E. Hoffmann and A. Saracz

Division of Building Research, CSIRO, Melbourne, Australia

Summary

The effect of tetramethyl thiuram disulphide (TMTD) as a fungicide has been assessed on panels coated with latex paints and exposed at Lae, New Guinea. The mould growth in each case was compared with that on a paint free of fungicide, and the loss of TMTD from paint films in Lae and in other locations was also determined.

TMTD was found to be of no great value in the humid climate prevailing in Lae. From the rate of disappearance of TMTD under various conditions it was concluded that paints containing this compound would be likely to show a mould resistance comparable with that of coatings containing pentachlorophenol or para-toluene sulphonamide if applied indoors.

Key words

Types of coating
latex coating

Biologically active agents
fungicide

Analysis, measurement and testing

Processes
weathering

Equipment
fog chamber

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

La mise au point de formules de peinture résistante à végétation mycelienne. Quatrième Partie: L'efficacité du disulfure de tétraméthylthiuram

Résumé

L'influence du disulfure de tétraméthylthiuram (TMTD) a été appréciée à l'aide des panneaux revêtus des peintures-émulsions et exposés à Lae, Nouvelle Guinée. La croissance de moisissure en chaque instance était comparée auprès de celle sur la même peinture exempte de fongicide. La perte de TMTD à partir des feuils de peinture exposés à Lae et aux autres emplacements a été déterminée également.

On a trouvé que le TMTD ne possède pas de valeur remarquable en tant que fongicide dans le climat humide régnant à Lae. En vue de la vitesse de disparition de TMTD sous des conditions diverses, on a conclut que des peintures contenant ce composé démontreraient vraisemblablement une résistance à végétation mycelienne comparable aux celles des revêtements contenant du pentachlorphénol ou de la para toluène sulfamide lors de leur utilisation à l'intérieur.

Die Rezeptur Pilzbeständiger Anstrichmittel: Zugabe von Tetramethylthiuramdisulfid

Zusammenfassung

An in Lae, Neu Guinea exponierten mit Latexfarben gestrichenenen Probetafeln wurde die Wirksamkeit von Tetramethylthiuramdisulfid (TMTD) als Fungizid bewertet. Der Schimmelbewuchs wurde stets mit dem auf fungizidfreiem Farbfilm verglichen, und der Verlust an TMTD aus den Farbfilmen in Lae und anderen Plazierungen wurde ebenfalls bestimmt.

Es wurde gefunden, dass TMTD in dem in Lae herrschenden, feuchten Klima wenig nützte. Aus dem Masse, in welchen TMTD unter verschiedenen Bedingungen aus dem Film verschwindet, wurde geschlossen, dass diese Verbindung enthaltende Anstrichmittel wahrscheinlich eine Pilzbeständigkeit aufweisen, welche mit solchen, die Pentachlorphenol oder Paratoluolsulfonamid enthalten, sofern in Innenräumen angewandt, vergleichbar sind.

Формуляция красок дающих защиту против плесени. 4: Добавление тетраметил-тиурам-дисульфида

Резюме

Оценивается влияние тетраметил-тиурам-дисульфида (ТМТД) как фунгисида на панелях покрытых латексоподобными красками и подверженных выветриванию на открытом воздухе в Лае, в Новой Гинее. Прирост плесени сравнивался в каждом случае с приростом на краске свободной от фунгисида и определялась также утеря ТМТД в красочных пленках в Лае и в других местах.

Найдено что ТМТД не представляет большой ценности во влажном климате преобладающем в Лае. Судя по скорости исчезновения ТМТД в различных условиях, сделано заключение что краски содержащие это соединение по всей вероятности обладают сопротивлением против плесени сравнимым с сопротивлением покрытий содержащих пентахлорфенол или паратолуол сульфонамид при применении в закрытом помещении.

Introduction

Tetramethyl thiuram disulphide (TMTD) has been proposed as a fungicide for latex paints[1], but apart from the bare assertion that it reduces mould growth on paint films there does not seem to be any information available as to its effectiveness. The Division of Building Research has received inquiries as to the usefulness of TMTD in paint, and it was decided to include this product in the current project on the formulation of fungus-resistant paints.

It has been pointed out[2] that the determination of the stability of a fungicide in a paint film exposed under similar conditions to those encountered in the field might help to provide an indication of its usefulness. The present paper deals with the loss of TMTD from paint films, and the performance of coatings containing it in a humid tropical climate which is very favourable to mould growth.

Experimental

Analytical Work

The latex paints containing 1, 2, and 3 per cent TMTD (on the liquid weight of the paint) and the corresponding blanks were brushed out on sheets (12in x 6in) of a polyethylene terephthalate polyester film which were then attached to asbestos cement panels and exposed under the following conditions:

(1) outdoors at Lae, New Guinea,

(2) outdoors at Highett, Victoria,

(3) in a fog room at 20°C,
(4) in a hot room at 38°C,
(5) in a constant temperature room at 20°C and 65 per cent RH

The panels at Highett were mounted on racks at an angle of 45° facing north; those at Lae had the painted films attached to both sides and were mounted at 45° facing 31° east of true north. The analytical method for determination of TMTD is described in the appendix. Three types of paint were used:

A. a latex paint based on acrylic resin with a pigment volume concentration of 40 per cent,
B. a gloss latex paint based on acrylic resin with a pigment volume concentration of 20 per cent,
C. a gloss latex paint based on a pva copolymer with a pigment volume concentration of 20 per cent.

The analytical results are summarised in Figs. 1, 2, and 3.

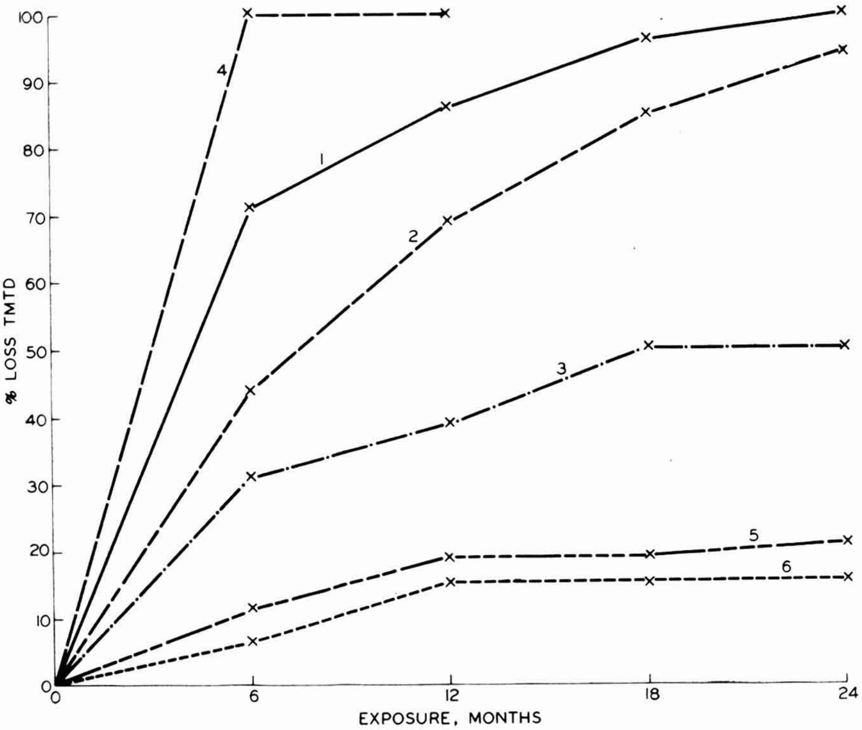

Fig. 1. Loss of TMTD from acrylic flat paint A originally containing 5.2 per cent TMTD.

1. Outdoors, Lae, New Guinea (upper side)
2. Outdoors, Lae, New Guinea (under side)
3. Outdoors, Highett, Victoria
4. Fog Room
5. Hot Room
6. Constant Temperature Room

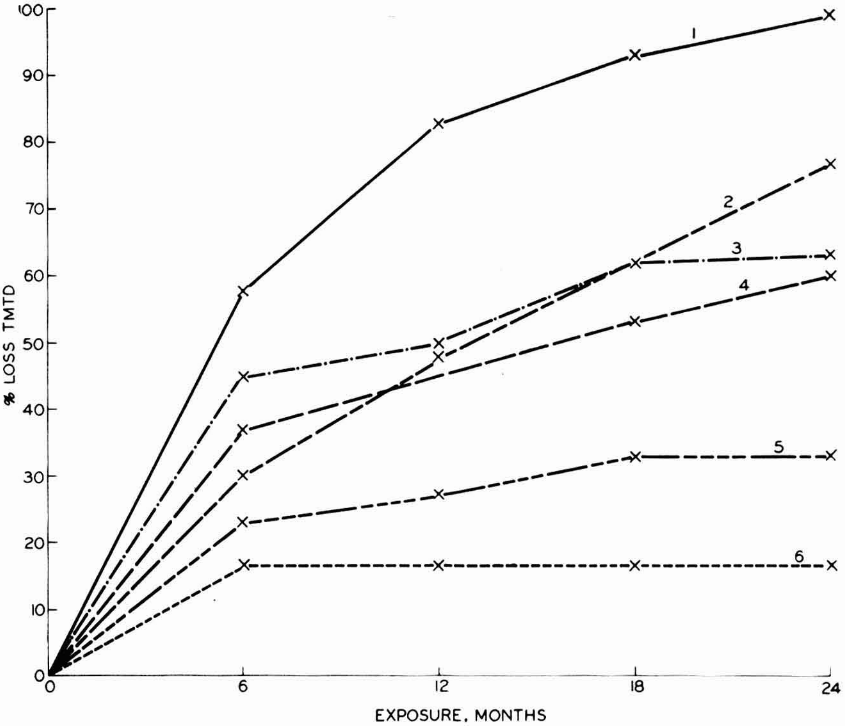

Fig. 2. Loss of TMTD acrylic gloss paint B originally containing 6 per cent TMTD

1. Outdoors, Lae, New Guinea (upper side)
2. Outdoors, Lae, New Guinea (under side)
3. Outdoors, Highett, Victoria
4. Fog Room
5. Hot Room
6. Constant Temperature Room

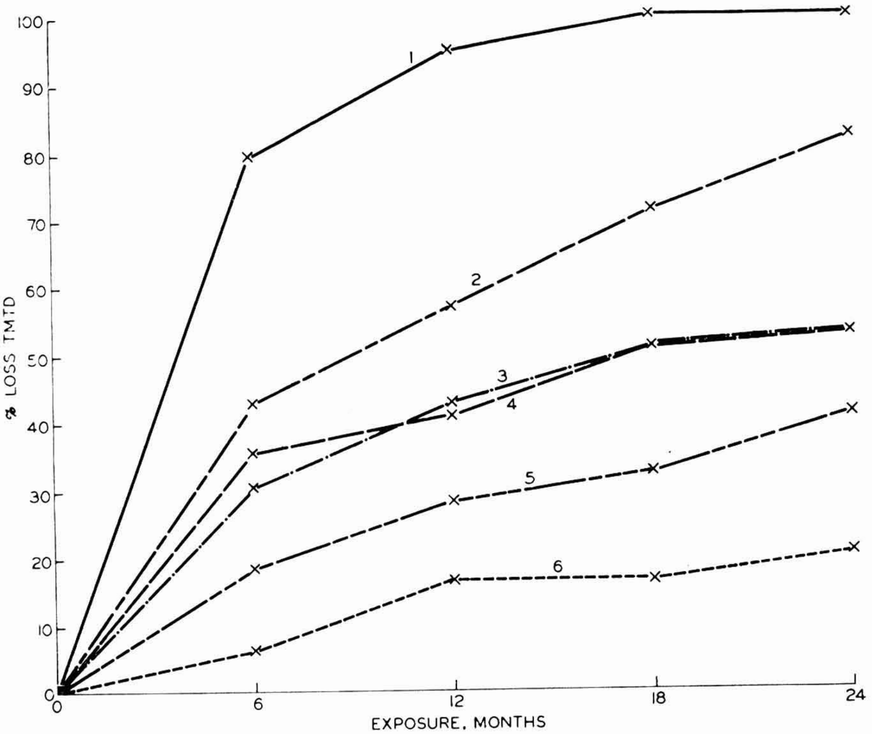

Fig. 3. Loss of TMTD from acrylic gloss paint C originally containing 4.9 per cent TMTD

1. **Outdoors, Lae, New Guinea (upper side)**
2. **Outdoors, Lae, New Guinea (under side)**
3. **Outdoors, Highett, Victoria**
4. **Fog Room**
5. **Hot Room**
6. **Constant Temperature Room**

Exposure at Lae, New Guinea

A separate set of asbestos cement panels was exposed at Lae, New Guinea. Both sides of each panel were painted with the paint under investigation, and the intensity and extent of mould growth on each side was assessed at intervals of about three months. The results of the assessments are shown in Tables 1 and 2.

Table 1

Assessment of mould growth on paint films exposed outdoors at Lae: Upper side of panel

Paint	TMTD %	Replicate	Exposure																	
			3 months		6 months		9 months		12 months		15 months		19 months		21 months		24 months		28 months	
			I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C
A	0	1, 2, 3	1	10	2	40	2	50	3	100	3	100	3	100	1–5	100	3–5	100	5	100
	1	1, 2, 3	0	0	0	0	2	5	2	5	2	5	2	100	2	100	3	100	3	100
	2	1, 2, 3	0	0	0	0	2	1	2	1	2	1	2	5	2	100	2	100	2	100
	3	1, 2, 3	0	0	0	0	2	1	2	1	2	1	2	5	2	100	1	100	2	100
B	0	1, 2, 3	0	0	2	10	3	30	3	100	3	100	3	100	5	100	4–6	100	5	100
	1	1, 2, 3	0	0	2	30	2	30	3	100	3	100	3	100	4	100	5	100	5	100
	2	1, 2, 3	0	0	2	30	2	30	2	100	2	100	2	100	3	100	4	100	3	100
	3	1, 2, 3	0	0	2	30	2	30	2	100	2	100	2	100	3	100	4	100	3	100
C	0	1, 2, 3	2	75	2	100	2	100	3	100	3	100	3	100	5	100	4–6	100	8	100
	1	1, 2, 3	2	75	2	75	2	100	2	100	2	100	3	100	4	100	4	100	7	100
	2	1, 2, 3	2	75	2	75	2	100	2	100	2	100	2	100	3	100	3	100	6	100
	3	1, 2 3	2 2	75 75	2 2	75 75	2 2	100 100	2 2	100 100	2 2	100 100	2 2	100 100	3 —	100 —	3 —	100 —	6 —	100 —

Each panel was assessed by noting the percentage area C covered by mould and by the colour intensity "I" according to the following scale: 9 black——→0 white

Table 2

Assessment of mould growth on paint films exposed outdoors at Lae: Under side of panel

Paint	TMTD %	Replicate	Exposure																	
			3 months		6 months		9 months		12 months		15 months		19 months		21 months		24 months		28 months	
			I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C
A	0	1, 2, 3	0	0	0	0	0	0	9	2	9	2	9	2	9	2	9	2	1	100
	1	1, 2, 3	0	0	0	0	0	0	9	1	9	2	9	2	9	2	9	2	1	100
	2	1, 2, 3	0	0	0	0	0	0	0	0	0	0	9	1	9	1	9	1	1	100
	3	1, 2, 3	0	0	0	0	0	0	0	0	0	0	9	1	9	1	9	1	1	100
B	0	1, 2, 3	0	0	0	0	9	1	9	5	4	25	1–9	100	1–9	100	1–9	100	1–9	100
	1	1, 2, 3	0	0	0	0	0	0	0	0	0	0	9	2	9	2	9	2	2	100
	2	1, 2, 3	0	0	0	0	0	0	0	0	0	0	0	0	9	1	9	1	1	100
	3	1, 2, 3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	100
C	0	1, 2, 3	0	0	0	0	0	0	9	1	3	20	3	30	3	30	3	30	1–9	100
	1	1, 2, 3	0	0	0	0	0	0	9	2	9	2	3	50	4	60	4	75	2–9	100
	2	1, 2, 3	0	0	0	0	0	0	0	0	0	0	0	0	9	1	9	1	1–9	100
	3	1, 2 3	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0	9 —	1 —	9 —	1 —	1–9 —	100 —

Each panel was assessed by noting the percentage area C covered by mould and by the colour intensity "I" according to the following scale: 9 black——→0 white

Discussion

The paint films exposed at Lae lost TMTD fairly quickly (Figs. 1-3, curves 1 and 2), and most of the fungicide (93 per cent or more) was lost from the upper side of the paint films in 18 months. The loss on the under side was slower at from 62 to 85 per cent in 18 months.

On the upper side, TMTD had an effect only in paint A (Table 3) and in paints B and C (both formulated to 20 per cent PVC) no effect could be noticed. The reason for this difference probably lies in the fact that paint films of a low PVC tend to retain matter blown on to them more easily than films of a high PVC[3]. Part of the material collected on the surface could be used by mould as food.

Table 3

Summary of mould growth assessments

Paint	TMTD %	Upper Side		Under Side	
		I*	II†	I*	II†
A	0	<3	<3	9	24
	1	6	6	9	24
	2	6	15	15	24
	3	6	15	15	24
B	0	3	3	6	9
	1	3	3	15	24
	2	3	3	19	24
	3	3	3	24	24
C	0	<3	<3	9	12
	1	<3	<3	9	15
	2	<3	<3	19	24
	3	<3	<3	19	24

*Column I—Length of time (months) in which all panels remained free of mould.

†Column II—Length of time (months) in which panels had less than 5 per cent coverage of mould.

All paints showed some improvement on the under side, but there was no appreciable difference in the growth of mould after 24 months.

At Highett, TMTD was lost from the paint film much more slowly than at Lae, the loss ranging between 50 and 67 per cent in 24 months. The much higher loss of TMTD in the fog room at 20°C compared with the losses in the constant temperature and hot rooms shows the importance of water in the decomposition of TMTD.

Conclusions

The addition of TMTD to latex paints does not increase their fungicidal resistance very appreciably in the humid tropics.

There was no opportunity to test the effect of TMTD in latex paints used indoors, but the comparative stability at 20°C, the lower loss on outside exposure in Highett, and a comparison with the rate of disappearance of pentachlorophenol[4], and para-toluene sulphonamide[5] (both of which decrease the growth of mould on interior paints), would all indicate that it is not unreasonable to conclude that 2 to 3 per cent TMTD added to paint would increase the mould resistance indoors for more than 3 years.

Acknowledgment

Thanks are extended to Mr G. Moss, a former officer of the Division of Building Research, for his assessments of the panels at Lae.

[*Received 21 October 1968*

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Appendix

Determination of TMTD in paint films

Principle

TMTD is extracted from the paint film with ethanol and the absorbance of the extracts measured at 275nm. The absorbance curve for concentration of 17.4 μg ml^{-1} is shown in Fig. 4.

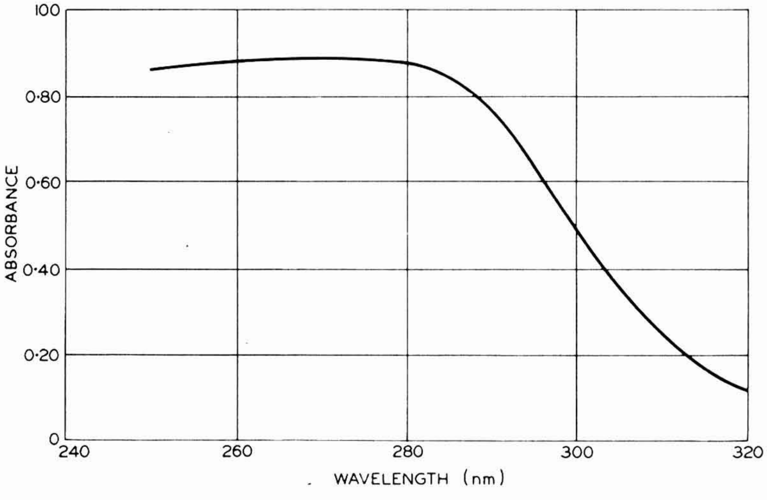

Fig. 4. Absorbance curve for tetramethyl thiuram disulphide in ethanol, concentration 17.4 μg/ml.

Practically all the TMTD can be extracted in one step, as can be shown by analysing the extracted paint film for residual sulphur.

Procedure

Extract 100 to 200mg of paint film in 20ml of ethanol under reflux for 2hr. Cool, separate the extract from the residue by centrifuging and make up to 25ml. Dilute a portion of the extract to obtain a solution containing from 5 to 25 μg ml^{-1}. As a blank use the extract from a similar quantity of paint film which has undergone the same exposure but is free from TMTD. Measure the absorbance at 275nm against the blank extract. In the concentration range from 0 to 30 μg ml^{-1} Beer's law is obeyed.

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The examination of the structure of antifouling coatings by scanning electron microscopy

By J. H. Bishop and S. R. Silva

Australian Defence Scientific Service, Department of Supply, Defence Standards Laboratories, Melbourne 3032, Australia

Summary

The recently developed scanning electron microscope yielded information of much more value in the study of antifouling paint films than was obtained from the conventional transmission instrument.

The significance of the information obtained is discussed and it is shown that current theories of the mechanism by which toxicant is released from the film require revision. Film porosity and surface texture, which are dependent upon the pigment loading, and also the wide variation in particle size and shape are shown to be important controlling factors. The critical pigment volume concentration is the parameter which determines whether or not a film is porous, rather than a pigment loading calculated on the assumption that the pigment particles can be regarded as uniform spheres as previously surmised.

The thickness of the layer of matrix material over the surface of the cuprous oxide particles and the degree to which the layer is ruptured, probably by osmotic pressure forces, also have a bearing on the rate of leaching.

Defects in antifouling paint films are easily detected.

A green patina observed on some surface areas of antifouling paint films removed from ships after service at sea is attributed to the presence of large numbers of diatoms and not necessarily to the presence of precipitated copper salts.

Key words

Types of coating	*Binders (resins etc)*	*Prime pigments*
antifouling coating	vinyl resin	copper oxide

Solvents
methyl isobutyl ketone
toluol

Processes primarily associated with

analysis, measurement or testing	*manufacturing or synthesis*
accelerated testing electron microscopy	leaching

L'investigation de la structure de peintures antifouling par microscopie électronique à balayage

Résumé

Le microscope électronique à balayage, récemment perfectionné, rendait des résultats beaucoup plus informatifs pour étudier les peintures anti-fouling que les résultats obtenus par l'instrument conventionnel à transmission.

On discute l'importance des résultats obtenus et l'on démontre que les théories actuelles du mécanisme de dégagement de l'agent toxique à partir du feuil doivent être revisées. La porosité de feuil et la texture superficielle, qui se dépendent de la teneur en pigment, et également la variation étendue de la grandeur et la forme du pigment se démontrent parmi les facteurs qui exercent une influence importante. Le pourcentage pigmentaire critique en volume est le paramètre qui détermine si le feuil soit poreux ou non, plutôt que la teneur en pigment calculée en supposant comme au préalable, que les particules soient sphèriques et uniformes.

L'épaisseur de la couche de matière enrobant la surface des particules de l'oxyde cuivreux, ainsi que le degré de rupture de cette couche, probablement par la pression osmotique, exercent une influence sur la vitesse de dissolution.

Die Untersuchung der Struktur von Antifoulings mit Hilfe der Abtast-Elektronenmikroskopie

Zusammenfassung

Das kürzlich entwickelte Abtast-Elektronenmikroskop lieferte wesentlich wertvollere Information für das Studium von Antifoulings, als dies mit dem konventionellen Transmissionsinstrument möglich war.

Die Bedeutung der erhaltenen Information wird besprochen, und es wird aufgezeigt, dass die gegenwärtigen Theorien über den Mechanismus, durch den Toxine aus dem Film freigemacht werden, der Revision bedürfen. Es wird gezeigt, dass Porosität und Oberflächenstruktur, die ihrerseits von der Höhe des Pigmentgehaltes abhängen, ebenso wie die grossen Variationen in Pigmentgrösse und -Form, wichtige, ausschlaggebende Faktoren darstellen. Die kritische Pigmentvolumenkonzentration ist der viel entscheidendere Parameter dafür, ob ein Film porös ist oder nicht, als die Pigmentfüllung, deren Berechnung auf der Annahme beruht, dass die Pigmentteilchen, wie bisher vermutet, als einheitliche Kügelchen anzusehen seien.

Auch die Dicke der sich auf der Oberfläche der Kupferoxidteilchen im Matrizenmaterial befindenden Schicht, und das Ausmass der wahrscheinlich durch osmotische Druckkräfte hervorgerufenen Durchbrüche in der Schicht, beeinflussen den Grad des Auslaugens.

Изучение структуры необрастающих покрытий при помощи растровой электронной микроскопии

Резюме

Недавно разработанный растровый электронный микроскоп принес более ценные данные для изучения необрастающих красочных пленок, чем данные полученные применением обычного оптического передаточного прибора.

Обсуждается значение полученных данных и показано что общепринятые теории механизма контролирующего освобождение токсического вещества из пленки, требуют ревизии. Показано что пористость пленки и поверхностная текстура, которые зависят от нагрузки пигмента, а также широкая вариация в величине и форме частиц, являются важными контрольными факторами. Критическая пигментная объемная концентрация является параметром определяющим пористость пленки скорее чем пигментная нагрузка, вычисляемая в предположении что пигментные частицы могут рассматриваться как однородные сферы, как это предполагалось прежде.

Толщина слоя матричного материала над поверхностью частиц закиси меди и степень до которой слой разрушается, по всей вероятности силами осмотического давления, также имеют отношение к скорости выщелачивания.

Introduction

Antifouling paints have been divided into matrix-soluble and matrix-insoluble types[1,2] according to the mechanisms thought to control the release of their toxic pigments into the surrounding seawater. If a paint film possesses a soluble matrix, toxicant buried in the film is exposed progressively to the leaching medium as the matrix dissolves, and thus is itself able to dissolve. In paint films possessing an insoluble matrix, seawater gains access to the toxicant buried in the film through cavities left by toxicant particles which have already dissolved. A few paints operating by a diffusion mechanism have also been reported[3], in which the matrix material swells when immersed in seawater, and the toxicant diffuses through the swollen, presumably gel-like, matrix.

The theories underlying this division into matrix-soluble and matrix-insoluble paints do not explain many of the phenomena observed in the study of antifouling compositions[4]. Most successful antifouling paint films possess matrices incorporating both soluble and insoluble materials and these paints, strictly speaking, cannot be placed in either category[5,6,7]. The theory of toxicant leaching for insoluble-matrix paints has been extended to cover this situation by assuming that all the soluble materials in such films behave as though they were in the form of uniform spheres embedded in an insoluble matrix[6].

In addition to the purely physical factors dealt with by the theories mentioned above, the rate at which the most widely used toxicant, cuprous oxide, is leached from antifouling coatings may depend upon the rates of the complex chemical reactions[8] involved in its solution in seawater, and the way in which these reactions vary with changing conditions.

At present, new antifouling paint systems have to be assessed over a long period of time, and the results obtained are far from reliable[7]. The theories already mentioned cannot be used to predict accurately the performance of antifouling paints from the chemical and physical properties of their constituents and also of the environment in which they are to be used. A quantitative theory capable of so doing would save much time and effort and would become increasingly useful as more synthetic materials, such as new organometallic toxicants and paint vehicles, become commercially available.

Current theories describing the action of antifouling coatings are based on models of their physical micro-structures deduced very largely from the properties of their individual constituents and from their toxicant leaching behaviour. They are derived partly, therefore, from the information which they seek to explain. It was therefore decided to examine the microstructures of antifouling coatings directly, so that a quantitative theory of leaching could be based upon data derived directly from the observation of film microstructure. The authors have so far concentrated their attention on coatings consisting of a soluble toxic pigment in an insoluble matrix, for which a quantitative theory has already been derived from first principles[9,10]. Transmission and scanning electron microscopy were employed in this study.

Experimental

Preparation of paint films

A range of antifouling paints containing different volume fractions of a commercial cuprous oxide pigment (Nordox cuprous oxide red, SG 6.0 g cm^{-3}) was prepared in the laboratory using an unplasticised vinyl resin (Union Carbide, VYHH grade) as the medium. These constituents were dispersed in a solvent consisting of 60 per cent by volume of methyl isobutyl ketone and 40 per cent by volume of toluol.

These laboratory-formulated paints were air-sprayed on to rigid vinyl panels, about twelve coats being applied to obtain the desired film thickness of approximately 100μm, with periods of 8-24hr between each coat to allow solvent to evaporate completely.

Some commercial antifouling paints were applied, using a doctor blade, to similar vinyl panels at a wet film thickness of about 80μm such as is likely in practice.

Samples from the hulls of two Royal Australian Navy Ships were also included in the investigation.

Accelerated leaching

Laboratory-prepared films were leached in an accelerated leaching solution consisting of an aqueous solution of sodium glycinate (0.025M) and sodium chloride (0.48M)[11]. The method of leaching used has been described previously[12].

Transmission electron microscopy

Various single stage and two stage replica methods were used to examine the paint film surfaces, but only single stage, metal-shadowed, carbon replicas were found to be of value for our purposes.

Scanning electron microscopy

Specimens of paint films for surface examination, approximately 5mm square, were mounted on metal stubs designed to fit the microscope specimen holder. A 4×10^{-8}m layer of gold was vacuum deposited on to each specimen while it was rotated to obtain an even coverage of gold. The gold layer was earthed to the stub using colloidal silver. The specimens were then examined using a Stereoscan Mark IIA microscope.

Surfaces for the examination of cross-sections through paint films were prepared after sectioning by means of a microtome first with a flat-bed microtome, then with an LKB ultramicrotome. These specimens were then coated and examined as described above.

Results and Discussion

Transmission electron microscopy

A typical transmission electron micrograph which was obtained from a replica of a laboratory-formulated paint film containing 68 per cent by volume of cuprous oxide, is shown in Fig. 1. Large areas of these replicas had a much more crumpled and distorted appearance than that shown, and replicas of the surfaces of leached films appeared to be even more distorted. Interpretation of these micrographs was very difficult, but the results indicated that the surfaces were rough textured[13,14], particularly after the pigment had been leached.

Direct transmission microscopy of thin sections microtomed from laboratory-formulated paint films was also found to be unsatisfactory.

The pigment particle sizes obtained with the transmission electron microscope showed that many features of the micro-structures of these films were beyond the resolving power of optical instruments[15], which also have a much smaller depth of field compared with scanning electron microscopes[16]. The latter instrument was therefore used for further investigations, an additional reason being its ability to examine rough-textured surfaces.

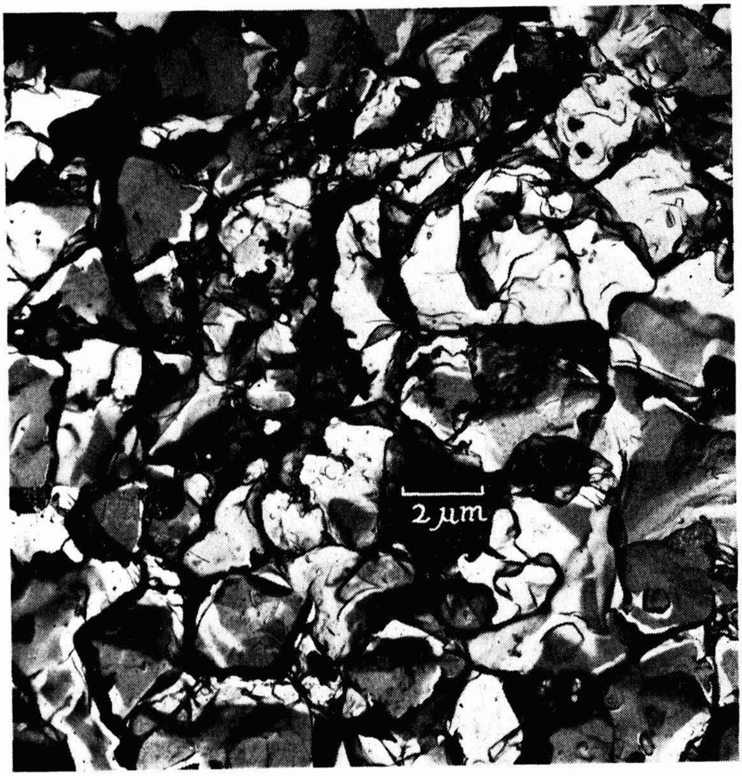

Fig. 1. Film containing 68 per cent cuprous oxide by volume, surface (transmission electron micrograph)

Fig. 2 is a scanning electron micrograph of the surface of a laboratory-formulated antifouling paint film similar to that shown in the transmission micrograph (Fig. 1). Features in the scanning micrograph are more easily recognized and evaluated than those in the transmission micrograph.

Scanning electron microscopy

Results of theoretical interest: Figs. 2 to 7 are scanning electron micrographs of laboratory-formulated experimental antifouling paint films, containing various volume fractions of cuprous oxide pigment, embedded in an insoluble vinyl resin matrix. A number of features of theoretical interest, which are discussed below, emerged from these micrographs and the large number of similar micrographs also examined.

Film porosity: The roughness and porosity of the surface of a film containing 60 per cent by volume of cuprous oxide, illustrated in Fig. 2, show that there is insufficient paint vehicle to fill the interstices between the particles although current theory[6] predicts that voids should only occur in films containing over 74 per cent by volume of pigment.

The surface of a paint film containing 30 per cent by volume of cuprous oxide, shown in Fig. 3, is much less porous than the surface of the 60 per cent

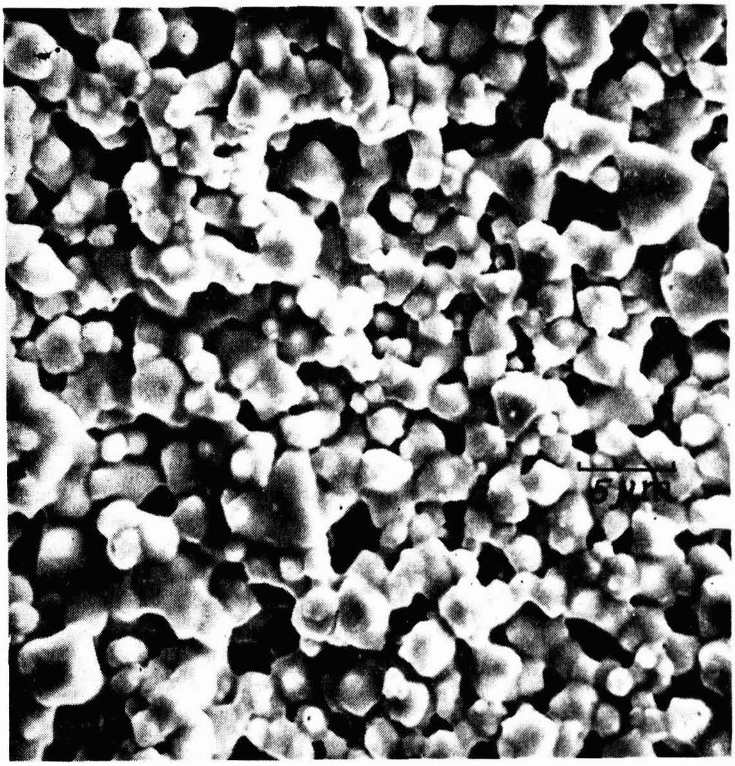

Fig. 2. Film containing 60 per cent cuprous oxide by volume, surface

pigment volume film illustrated in Fig. 2. Examination of the surfaces of a number of paint films with different volume fractions of cuprous oxide has shown that there is a steady progression from smooth, non-porous surfaces at low volume fractions to rough, porous surfaces at high volume fractions.

Differences in film porosity, resulting from different pigment loadings, will affect the leaching rate of toxicant from matrix-insoluble coatings if it is assumed that leaching rate is controlled by the physical structure of the film. The more porous the film, the more readily dissolved toxicant and unreacted leaching agent will be able to diffuse through the honeycombed, already leached, surface layer. In addition, the more porous the film the more readily the leaching medium will be able to permeate the unleached part of the film, thus increasing the effective area from which toxicant can dissolve. Micrographs of cross-sections through films indicate that this penetration occurs, but the leaching rate could be controlled entirely by the rate at which the toxicant is released into the leaching medium through the leached layer of the film. Thus the increased porosity of antifouling coatings with increased pigment loading may increase the toxicant leaching rate throughout the life of the coating to a greater extent than would occur if the antifouling coatings were uniform and non-porous.

Surface texture: The initial toxicant leaching rate should be directly proportional to the area of cuprous oxide exposed to leaching and hence to the volume

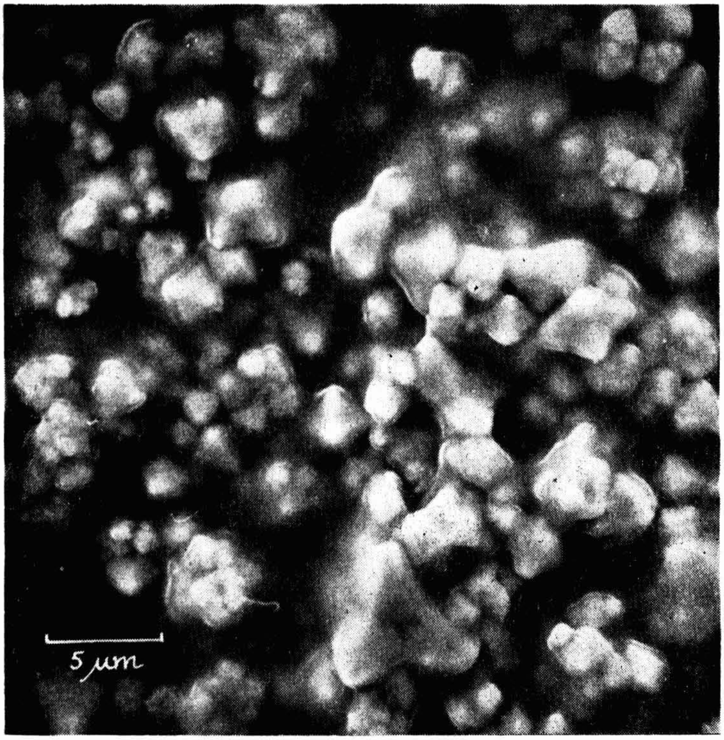

Fig. 3. Film containing 30 per cent cuprous oxide by volume, surface

fraction of pigment[17], provided that the film surface structure does not vary with pigment content and that the flow of the leaching medium past the surface is sufficient to remove the toxicant as it dissolves. However, comparison of Figs. 2 and 3 shows that, in addition to porosity, surface texture is also a function of the volume fraction of pigment. Examination of a number of coatings showed that film surfaces become rougher in texture as the pigment loadings increase. This is in accordance with the findings of workers using other types of paint[18].

A rough-textured film exposes a greater area of toxicant to the leaching medium than a smooth-textured film of the same nominal surface area. The initial toxicant leaching rates of rough-textured films should therefore exceed those of smooth-textured films to a greater extent than expected from their respective volume fractions of pigment, provided that the flow of leaching solution adjacent to film surfaces is not affected by differences in surface texture.

The raised areas of rough-textured antifouling film surfaces are leached faster than those surface areas lying further into the film which appear to be more protected from the action of the leaching medium. This is seen in Fig. 4 and similar micrographs of the surfaces of a number of laboratory-formulated antifouling paint films after a short period of leaching. Breaches in the surface coating of matrix material show clearly where leaching has occurred. Thus the region of the film from which toxicant is being leached will become increasingly laminar as leaching continues and the effect of surface texture

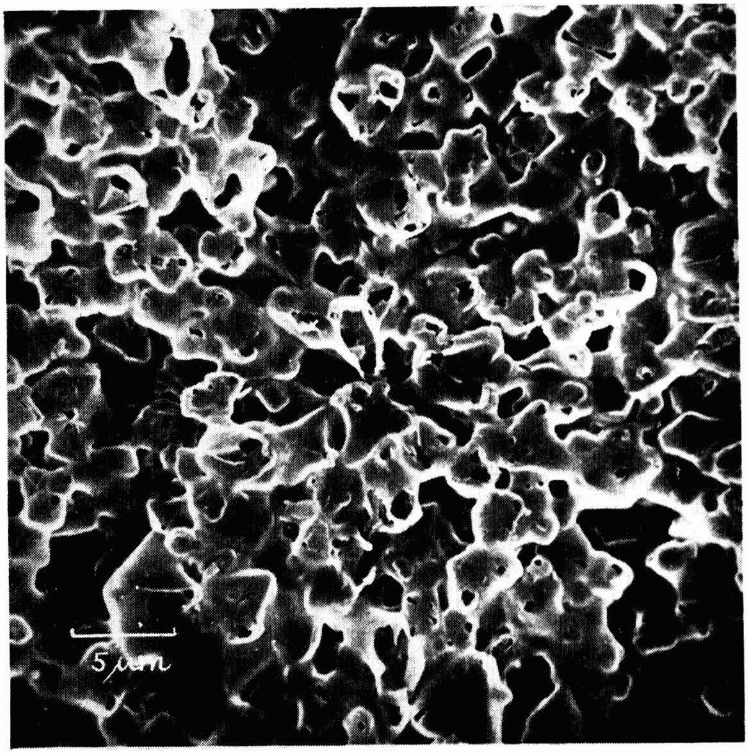

Fig. 4. Film containing 60 per cent cuprous oxide by volume, surface after 45hr experimental leaching

should become less important, so that only the initial leaching rates should be affected significantly.

Packing of pigment particles: Transmission electron microscopy of the dry pigment[19] had shown it to consist of angular particles which tended to be almost cubic in shape with rounded edges and corners. These particle shapes are clearly seen in Fig. 2, the particles ranging in size from 0.1 to 12μm diameter.

The non-spherical shapes of the pigment particles and the wide range of particle sizes offer an explanation of the greater porosity of the film illustrated in Fig. 2, containing 60 per cent by volume of cuprous oxide, compared with that predicted by theories which assume that the particles can be regarded as uniform spheres in direct contact. Results obtained with iron oxide pigmented films[20] showed that the critical pigment volume concentration is the parameter which determines whether or not a film is porous. The critical pigment volume concentration is different for different pigments and is not the 74 per cent calculated from the packing of uniform spheres. In addition, some matrix materials may coat pigment particles in such a way as to prevent particle to particle contact, thus increasing the effective volume of pigment relative to the volume of free matrix material available for filling the voids.

Fig. 5 shows a vertical cross-section through a film containing only 34 per cent by volume of cuprous oxide. Even at this low pigment loading many cuprous oxide particles are in contact with each other.

Fig. 5. Film containing 34 per cent cuprous oxide by volume, vertical cross-section

The effect of leaching on the insoluble film matrix: Fig. 6 is a micrograph of a cross-section, normal to its surface, through a paint film which had contained 60 per cent by volume of cuprous oxide before being subjected to accelerated leaching and clearly shows the interface between the leached and unleached parts of the film. Examination of a large number of micrographs of the leached parts of this and similar films has shown that the cavities left by solution of the cuprous oxide particles are interconnected. The matrix material has not been visibly affected by immersion and complete leaching has occurred to a uniform depth.

Although many of the apertures which interconnect the cavities left by leaching are irregular in shape and due to direct contact between pigment particles, others are rounded and could be the result of the rupture of the matrix material encapsulating some pigment particles. It has been postulated[10] that rupturing is caused by osmotic pressure developing at the vinyl resin-cuprous oxide interface when cuprous oxide particles start to dissolve.

Further information about the rupturing of matrix material encapsulating pigment particles is provided by the examination of paint film surfaces. Figs. 2 and 3 show that the surface pigment particles are covered by a thin layer of paint vehicle. The different leaching characteristics[21] of antifouling paint films leached as prepared, compared with those of films leached after wet-

Fig. 6. Film containing 60 per cent cuprous oxide by volume, vertical cross-section after leaching

grinding their surfaces on fine carborundum paper, can now be attributed to the existence of this thin coating over the surface particles.

Micrographs of leached paint film surfaces, such as Figs. 4 and 7, show that the network of cavities in the leached part of a paint film opens directly on to the film surface. The thin coating of matrix material covering surface pigment particles is therefore breached in the course of leaching. Both these specimens were leached under identical conditions, but the layer of matrix material covering the surface of the film containing 30 per cent by volume of cuprous oxide (Fig. 7) has been breached to a far smaller extent than the film containing 60 per cent (Fig. 4). The breaches in the film with the lower pigment loading are much smaller than those in the film with the higher pigment loading, suggesting that the surface coating of matrix material is much thicker for the film with the low pigment loading and is therefore more difficult to breach.

Since the thickness of the layer of matrix material over the surface cuprous oxide particles is dependent upon pigment loading, this is another factor, in addition to surface texture, which is controlled by the pigment content of the film and which will affect the initial rate of leaching of toxicant from insoluble-matrix antifouling coatings. The appearance of the holes in the film surfaces produced by leaching is suggestive of their formation by osmotic pressure rupture rather than by solution or erosion of the matrix material.

Commercial antifouling paint films

The surfaces of eight commercial, cuprous-oxide pigmented, antifouling coatings were examined before and after leaching. The volume fractions of cuprous

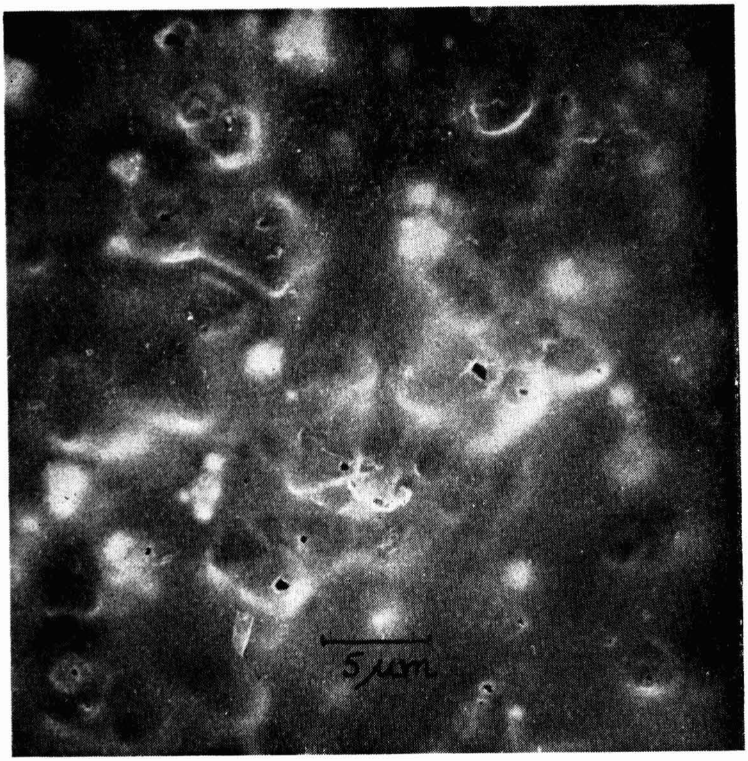

Fig. 7. Film containing 30 per cent cuprous oxide by volume, surface after 45hr accelerated leaching

oxide in all these films were between 25 per cent and 50 per cent indicating that most, if not all, contained soluble matrix components. Fig. 8 shows the surface of one of these coatings containing about 30 per cent by volume of cuprous oxide before leaching. The smooth-textured surface typical of coatings with low pigment loadings is clearly seen. Fig. 9 is a high magnification view of the surface structure of the film after leaching. The rounded appearance of the remaining matrix material and the shapes of the cavities themselves, shown in this and other micrographs, indicated that an appreciable amount of the paint vehicle had dissolved.

With most of these films a sponge-like structure of insoluble material is left after the soluble constituents have dissolved, supporting the view[6] that most commercial paints correspond more closely to the "contact leaching," insoluble matrix, category of antifouling paint than to the matrix soluble type. However, Fig. 10 shows a film which has been partly leached by the "matrix-soluble" mechanism; the film surface before leaching was very similar in appearance to that shown in Fig. 8. The matrix material has dissolved uniformly to expose the cuprous oxide particles, giving a so-called[22] "pebble-dash" appearance, no skeleton of matrix material remaining after the cuprous oxide has dissolved. Partington and Dunn[22] have discussed how the topography of the "matrix-soluble" type of film may vary with the conditions of leaching. Under some conditions the cuprous oxide pigment may dissolve more rapidly

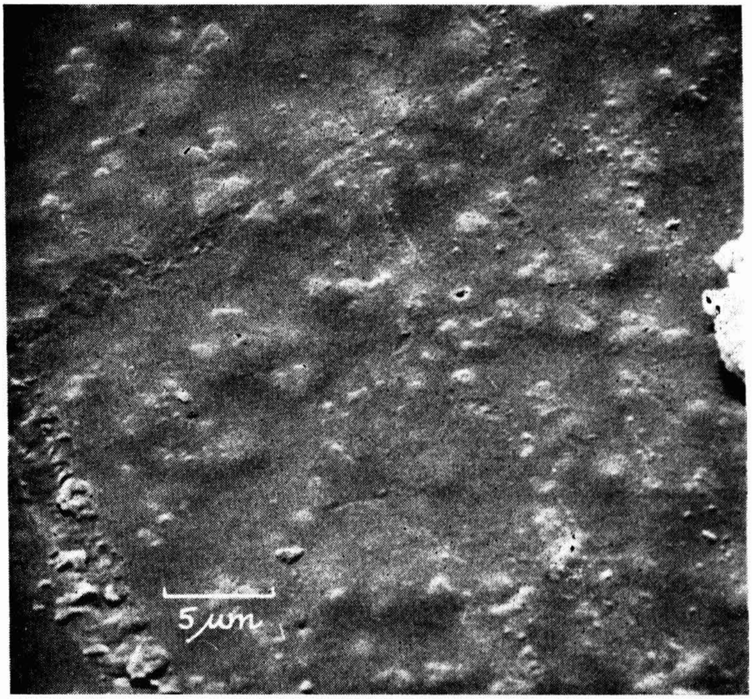

Fig. 8. Commercial coating with "cold plastic" matrix, surface tilted 45°

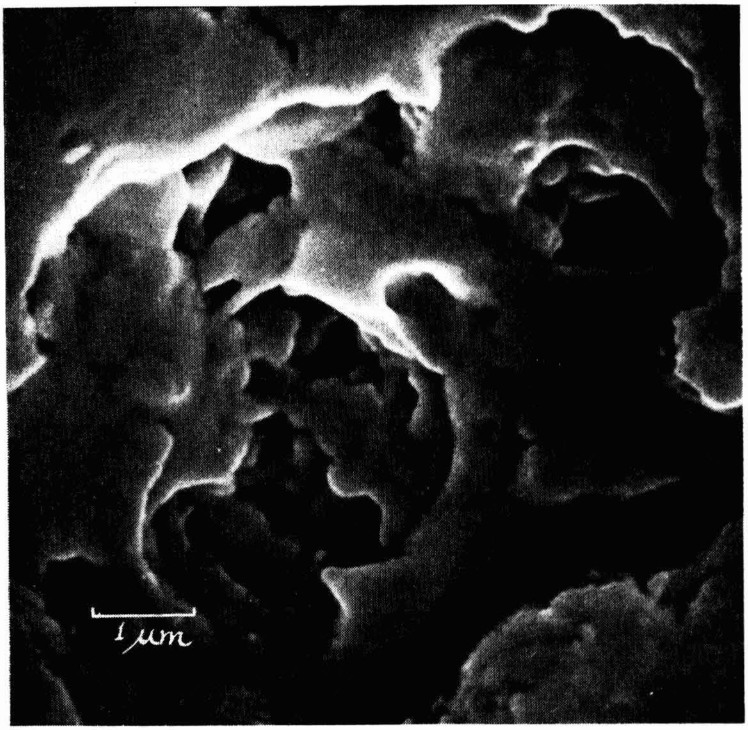

Fig. 9. Commercial coating with "cold plastic" matrix, surface after leaching

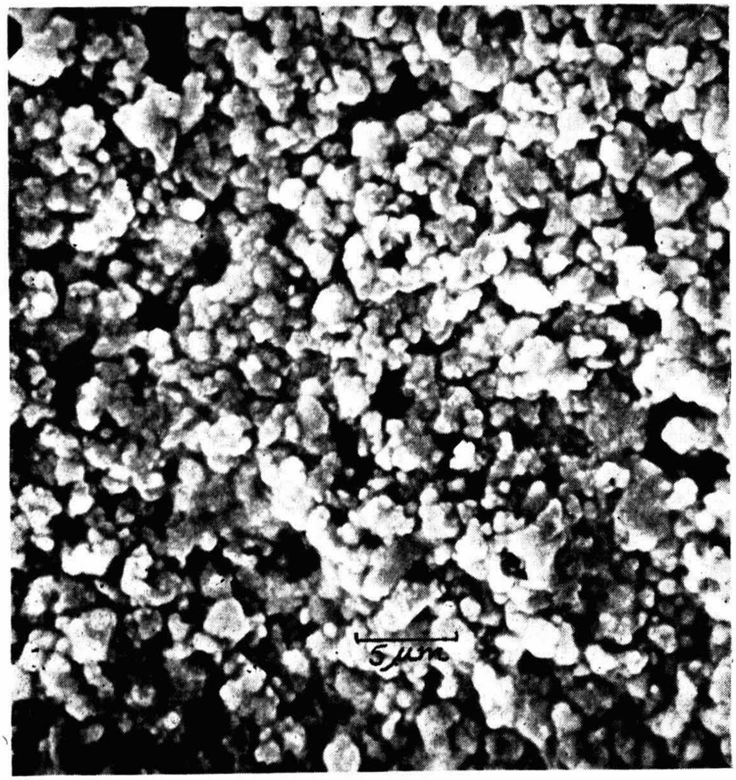

Fig. 10. Soluble-matrix commercial coating, surface after leaching

than the matrix material. The leached film would then have a similar appearance to that of an insoluble matrix paint. Information gained with the scanning microscope to determine the mechanism by which leaching has occurred should therefore be treated with circumspection.

The detection of flaws

The scanning electron microscope has proved useful for detecting flaws in antifouling coatings. Fig. 11 shows a hole in the surface of a leached, laboratory-formulated, film which was one of a large number found in this specimen. These holes are the surface manifestation of small spherical cavities believed to be caused by air entrapped during the application of the paint under unsuitable conditions. The holes increase both the surface area of the film and the ease of leaching from within the film. Erroneous conclusions could therefore be drawn from leaching rate determinations made using such films and it is advisable to select films that are, as far as possible, free from flaws.

Fig. 12 shows the surface of a cuprous oxide pigmented, epoxy ester based, commercial antifouling coating before leaching. The flaws in this film, consisting of small holes, frequently interconnected in a network of fine cracks, are so numerous that they are probably a necessary feature contributing to the anti-

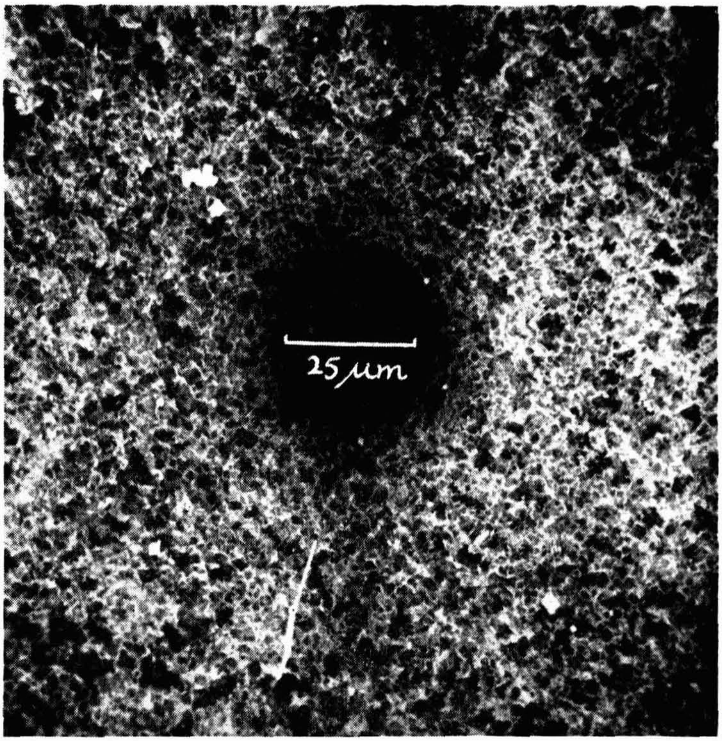

Fig. 11. Film containing 80 per cent cuprous oxide by volume, surface after leaching

fouling effectiveness of this paint. Micrographs at 0° tilt and at higher magnifications show the cracks in greater detail. The coating does not fail mechanically in service, probably because of the tough epoxy binder.

Specimens from ships

Fig. 13 shows the surface of an antifouling paint film sampled after about one year's service on a destroyer. Diatoms, with a population density of 750,000 organisms per square cm, are clearly shown both on the surface and in the cavities leading from it. Useful information could not be obtained with optical microscopes. Adjacent areas of this film had retained the colour of the cuprous oxide pigment and were almost devoid of marine organisms.

Samples of antifouling coating removed from another vessel after six months' service had a surface speckled with bright green patches of the order of 5mm diameter. The scanning microscope showed that these green areas were thickly covered with diatoms, population density 3×10^6 organisms per square cm, which were seen to be different to those on the specimen described above. The green surface colouration of these paint film samples was therefore associated with the presence of colonies of diatoms.

Diatoms have been found on some antifouling coatings soon after immersion and comprise an important part of the "primary slime" which forms on submerged surfaces prior to the attachment of macro-fouling organisms[23]. However,

Fig. 12. Commercial coating with epoxy ester matrix, surface tilted 45°

many of the sessile species of diatoms which might be expected to form the main part of these colonies are dark brown in colour although free-floating planktonic diatoms are greenish-yellow in colour[24]. The brown pigmentation of the sessile species is due to a mixture of chlorophylls, xanthins and carotenes[24]. Chlorophylls and similar compounds react readily with copper ions to give strongly coloured bluish-green complexes[25]. Diffusing copper ions from antifouling coatings are thus likely to react with these compounds to produce the green colourations observed.

De Wolf and van Londen[7] have found that a bluish-green deposit forms on insoluble matrix films but not on those with soluble matrices. They also pointed out that the composition of this copper-containing deposit is still unknown because, although some authorities believe it to consist of basic copper carbonate, they themselves were unable to detect the presence of any carbonate group in the deposit. The continually eroding surfaces of matrix-soluble coatings would prevent the development of colonies of diatoms. Thus the green colouration which develops on antifouling surfaces might often be due to the presence of diatoms and not to deposited basic copper carbonate or other insoluble inorganic copper compounds.

In addition to colouring the film green the diatoms modified the surface topography considerably and would physically obstruct the release of toxicant from the film. However, the "primary slime" of which they form a major

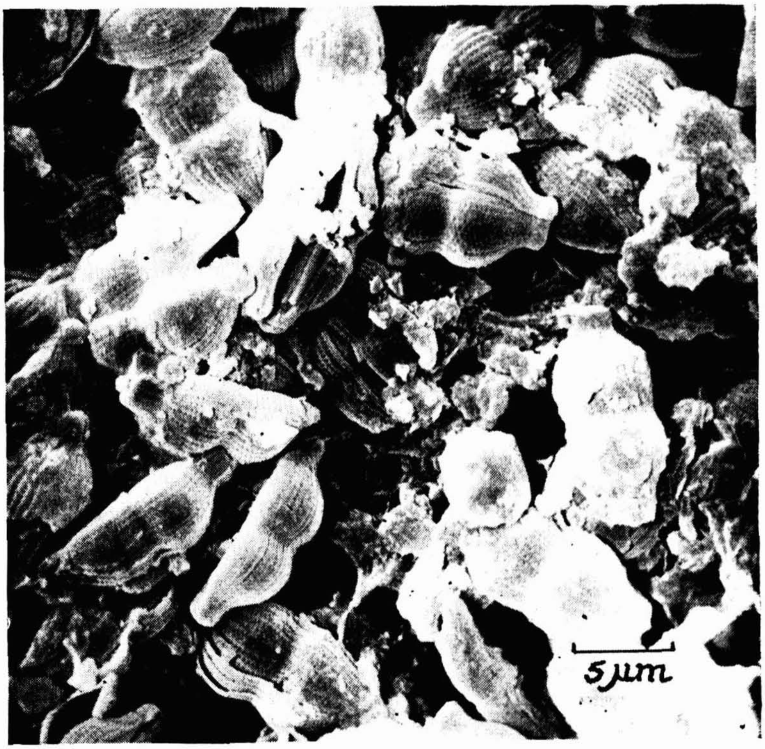

Fig. 13. Antifouling coating from a destroyer, surface after service

part frequently has a pH considerably lower than that of the surrounding seawater[23]. The solubility of cuprous oxide in seawater is directly proportional to the hydrogen ion concentration[8] and therefore will be greater in the slime; this may increase the rate at which cuprous oxide is leached.

The presence of large numbers of microfouling organisms, alive or dead, on the film surface may encourage macro-fouling to develop by providing a substrate for further settling[26].

Conclusions

Scanning electron microscopy can be used to obtain information about physical features of antifouling paint films which are often beyond the resolving power of optical microscopes. Conventional transmission electron microscopy is much more difficult to apply to the examination of these films and offered no advantages in the present investigation.

The scanning electron microscope reveals flaws in antifouling coatings very clearly. It is of interest that one commercial coating exhibited features normally described as flaws which could well, unknown to its formulator, be responsible for its good performance. The instrument can also provide information as to the solubility or otherwise of the film matrix.

Specimens of antifouling coatings removed from two ships after service at sea showed that microfouling organisms can be studied *in situ* and in great detail with the scanning microscope. The green colouration of some surface areas of these coatings is probably due to colonies of diatoms and not necessarily to precipitated copper salts as previously suggested. These may also influence the release of toxicants from the film.

Examination of cuprous oxide pigmented paint films with the instrument has revealed details of film micro-structure, not previously amenable to direct examination, having a direct bearing on the toxicant release mechanism. Features of interest are the increased porosity and increased roughness of surface texture with increased pigment loading and the presence of a thin, continuous, layer of insoluble matrix material covering the surface pigment particles, which ruptured in the course of leaching, apparently by an osmotic pressure mechanism. The thickness of this layer decreased with increasing pigment content. Finally, the non-uniform sizes and shapes of the pigment particles are clearly revealed and the authors suggest that film porosity and surface texture are better explained in terms of critical pigment volume concentration than by assuming that the pigment particles exhibit the same packing behaviour as uniform spheres.

Established theories do not take account of these features and it is hoped to place the qualitative information so far obtained on a quantitative basis to assist in the elucidation of the mechanism by which antifouling paints operate.

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The use of an electrical resistance method for investigating the performance of polymer coatings

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Summary

The testing of polymer coating films by an electrical resistance method is described and comparisons are made of the behaviour of certain typical varnish materials under acid and alkaline conditions. Correlation of the results with cation permeability, obtained by radiotracer techniques, has been attempted. The implications of the resistance changes and of the permeability results are discussed.

It has been shown that alkyds and oleoresinous materials are degraded in even mildly alkaline conditions, whereas polyurethane and epoxy-polyamide systems are relatively stable to strongly alkaline solutions. It is concluded that the resistance method is suitable for establishing the vulnerability of polymer films to certain specific environments.

Key words

Types of coating
alkyd coating
epoxy-ester coating
urethane finish

Processes and methods associated with analysis and testing
electrical resistance test
radiation chemistry

Binders—resins etc.
alkyd resin
amide resin
congo resin
epoxy resin
oleoresin
phenolic modified alkyd
styrenated alkyd
urethane resin

—oils etc.
linseed oil

L'utilisation d'une méthode de résistométrie électrique pour investiger le rendement des revêtements polymères

Résumé

On décrit l'épreuve des feuils de revêtements polymères par une méthode de résistométrie électrique, et l'on considère le comportement, sous des conditions acides ou alcalines, de certains composés des vernis communs. On a tenté de faire une corrélation des résultats avec la perméabilité cationique obtenue par la technique de radiotraçage. On discute les implications des changements de résistance et également celles des résultats de la détermination de perméabilité.

On a démontré que les résines alkydes et les vernis gras sont dégradés sous des conditions d'alcalinité légère, tandis que les systèmes à polyuréthan ou à époxy-polyamide sont rélativement stables aux solutions fortement alcalines. On conclut que la méthode de résistométrie électrique est convenable pour déterminer la sensibilité des feuils de polymères aux certains milieux specifiques.

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Die Anwendung einer elektrischen Widerstandsmethode zur Untersuchung des Verhaltens von Überzügen aus Polymeren

Zusammenfassung

Die Prüfung von polymeren Anstrichfilmen unter Verwendung einer elektrischen Widerstandsmethode wird beschrieben, und Vergleiche werden gezogen hinsichtlich des Verhaltens gewisser typischer Lacke unter sauren und alkalischen Versuchsbedingungen. Es wurde versucht, Korrelation der Resultate mit Kationendurchlässigkeit mittels Radiotracertechniken zu erhalten. Die sich daraus für die Änderungen der Widerstände, sowie Durchlässigkeitsresultate ergebenden Folgen werden besprochen.

Es wurde aufgezeigt, dass selbst unter mild alkalischen Bedingungen Alkyde und Materialien auf Ölbasis abgebaut werden, während Polyurethan-Systeme und Epoxy-Polyamidsysteme gegenüber stark alkalischen Lösungen verhältnismässig stabil sind. Das Ergebnis der Versuche zeigt, dass die Widerstandsmethode sich zur Feststellung der Empfindlichkeit von Polymerfilmen unter manchen spezifischen Einwirkungen am besten eignet.

Применение метода электрического сопротивления в изучении характеристик полимерных покрытий

Резюме

Описывается испытание пленок полимерных покрытий методом электрического сопротивления и делается сравнение поведения некоторых типичных лаковых материалов в кислых и щелочных условиях. Делается попытка соотнести полученные результаты с данными катионной проницаемости, полученными на основе радиоактивной техники. Обсуждается значение изменения сопротивления и результатов проницаемости.

Показано что алкиды и олеосмольные материалы деградируются даже в слабощелочных условиях, в то время как полиуретан и эпокси-полиамидные системы сравнительно устойчивы в сильных щелочных растворах. Делается заключение что метод сопротивления пригоден для определения уязвимости полимерных пленок в некоторых специфических окружающих условиях.

Introduction

General

Constituents of the service environment to which organic coatings may be exposed can attack specific bonds or groups in the macromolecules. The current wide choice of coatings for such conditions calls for rapid and reliable screening tests to select the more durable materials. Methods which reveal the degradation mechanisms of polymer films in these specific attacks would be even more valuable. They would provide greater understanding of the factors likely to increase rates of polymer failure and the possibility of controlling the response to the environment to the best advantage[1].

Accelerated weathering tests are widely used for durability assessment[2] but, with the more resistant materials now available, they are comparatively slow and the mechanisms of degradation are by no means adequately understood. Exposure conditions are somewhat inflexible and correlation with natural weathering behaviour becomes less certain with the more durable coatings.

The aims of the work described were:

1. to evaluate an alternative and more rapid procedure which might be used with greater flexibility than weathering tests for special conditions of exposure,
2. to compare the behaviour of some typical varnish media under the selected test conditions,

3. to determine the influence of water and ions which may penetrate and cause deterioration of the film, leading to corrosion or damage to the substrate.

Choice of method

The nature of the corrosion and the factors controlling it have greatly influenced the choice of methods of investigation, since the protection of metals, especially ferrous metals, is one of the foremost uses for organic coatings.

Corrosion of metal in aqueous media is an electrochemical process in which the formation, activity and movement of ions play important parts. The formation of corrosion cells with discrete anodic and cathodic areas and the function of oxygen in the process has been well established[3]. In the case of iron, iron (II) ions, formed at the anode, and hydroxyl ions, resulting from the oxygen depolarisation reaction at the cathode, diffuse through the electrolyte and interact to produce iron (II) hydroxide. Further action of oxygen produces finally the complex hydrated iron (III) oxide, rust.

An unpigmented polymer coating on a metal substrate will slow the corrosion process by virtue of the high resistance which it interposes between anodic and cathodic areas. Limitation of oxygen and moisture penetration to the metal will reduce or prevent the cathodic reaction, but permeability measurements have shown that coatings in practice allow sufficient diffusion to support a corrosion process[4,5,6]. Films have also been shown to vary in permeability to other agents, e.g. ions[7,8]. The degree of protection that coatings afford is thus dependent on their resistance to attack and penetration. Hence it is likely to be related to their electrical resistance in a given environment.

Measurements of changes in the electrical properties of films, e.g. capacitance[9], electrophoretic mobility[10] and resistance, have been reported. The behaviour of certain types of coating film has been investigated by Mayne and his colleagues[11,12,13] in circumstances where the resistance changes of polymer films could be related to their electrolyte environment. Bacon, Smith and Rugg[14] have examined the electrical resistance of films in sea water and have stated that those with a resistance of less than about 10^6ohm cm^{-2} have little protective effect in such conditions. They found that values greater than 10^8ohm cm^{-2} were required for satisfactory behaviour. Bratt[15] has also used an electrical resistance method to indicate the failure of coatings exposed to alkaline conditions.

The use of radiotracers in following the permeability of water and ions through films has been described[16,17,18] and it was therefore decided to use the isotope, ^{42}K, to complement resistance measurements in investigating the movement of cations. The permeability results were supplemented by the preparation of autoradiographs from treated films.

Experimental

Apparatus for resistance measurements

The apparatus and techniques used were similar to those described by Maitland and Mayne[11] (Fig. 1). The standard resistors, Rs, were a carefully calibrated decade series with values ranging from 10^5 to 10^{12} ohm. The resistance of the electrometer was greater than 10^{13} ohm and inaccuracies due to non-linearity of the instrument and circuit relationship began to appear if films beyond 10^{12} ohm resistance were tested.

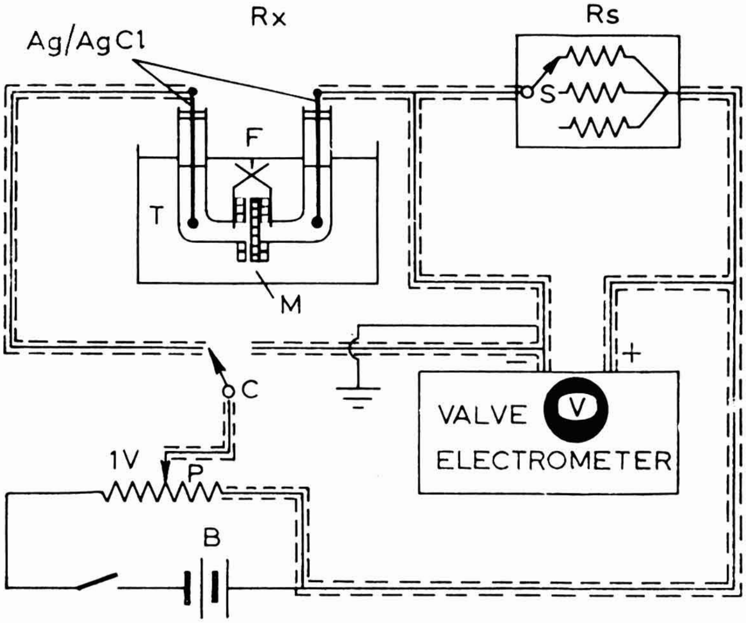


Fig. 1. Circuit and component details

The film under test was mounted as a 13mm diameter membrane, M, in the electrolytic cell between two silver/silver chloride electrodes. It is important that the latter should behave reproducibly, this being ensured by careful selection from batches prepared in the laboratory[19], by frequent checking to see that the potential differences between electrodes was within a 5mV limit, and by mounting in fixed locations in the cell limbs. A potential of 1,000mV was applied across the cell and the potential drop compared with that across the known resistance.

Preparation and mounting of coating films

A rigorous procedure was used to prepare unpigmented detached films. Each varnish medium was strained through a pad of No. 1 Whatman paper, in a disposable hypodermic syringe, on to prepared glass plates and spread by doctor blade to give a 50 micron (μm) wet film thickness. The use of a glove box or dust cover is essential to prevent the deposition of dust[20]. Alkyd and oleo-resinous films were air-dried at room temperature for 24 hr followed by oven-drying for 12 hr at 60°C. Chemically-cured films were air-dried at room temperature for 12 hr followed by oven-drying for 6 hr at 60°C.

Films were stripped from the glass plates after soaking in water, washed, dried and cut into discs of uniform thickness, free from visible defects. In some cases, treatment of the glass plates with a thin film of soluble cellulose[21] during their preparation was used to facilitate stripping of the film on wetting.

The electrolytic cells were treated with dimethyldichlorosilane, to minimise electrical leakage, the flange joints warmed to soften the wax sealant previously applied and the 13mm diameter film disc inserted and sealed at the flange edges. At least six identical cells were prepared for each test.

Conditioning and resistance measurement technique

The mounted films were conditioned in 0.001N HCl for a period of 18 hr at 25°C. The cells were subsequently rinsed with distilled water and then filled with the test solution. In this investigation, the effect of pH has been chiefly studied.

Sets of films were brought to equilibrium[11] by treating for 5 hr at 60°C with each of a range of buffers between pH 2.0 and pH 13.0, containing only hydrogen and potassium cations[22]. The cells were then cooled, rinsed out with glass-distilled water and refilled with potassium chloride (0.001N, 0.1N or 3N) on each side of the membrane. Resistances were measured at 25±0.05°C.

In making the measurements, silver-silver chloride electrodes, previously held at the temperature of measurement, were positioned in the electrolyte in the cell limbs. As the system approached equilibrium, electrometer readings were taken at regular intervals until they became steady. The electrode positions were then reversed, further readings taken and the mean value calculated.

Radiotracer methods

When making permeability measurements, ^{42}KCl, of the concentration used in resistance measurements, was placed in one limb of the resistance cell and samples taken by micro-pipette from the opposite limb. The planchette counting technique was used. In further tests, the tracer was incorporated in the buffer conditioning solutions.

On dismantling the test cells, the varnish films were examined, counts of absorbed ^{42}K made and autoradiographs prepared. The technique was to position a sample of detached film, after washing in distilled water, on a gelatine coated glass plate. Photographic film strip was placed over the specimens in the dark room and covered by another glass plate. The exposure "sandwich" was finally bound with sealing tape and placed within lead shielding for the exposure period, usually of several days' duration.

Coating materials

In the investigation reported here the following unpigmented varnish media were examined:

1. styrenated alkyd.
2. linseed glycerol alkyd.
3. pure phenolic alkyd.
4. epoxy ester.
5. linseed pentaerythritol alkyd.
6. oleoresinous linseed/congoester.
7. epoxy-polyamide: A. epoxy resin (42 per cent solids) 4 parts vol.
   B. polyamide (55 per cent solids) 1 part vol.
8. polyurethane: A. polyurethane base (40 per cent solids) 2 parts vol.
   B. polyurethane accelerator (92 per cent solids) 1 part vol.

Results

Resistance of films conditioned at various pH values

Resistance results obtained at 25°C, with 0.001N KCl in the cells are shown in Fig. 2. They show the resistance of films which had been conditioned as described above at pH values between 3.0 and 13.0. The results measured in 0.1N KCl

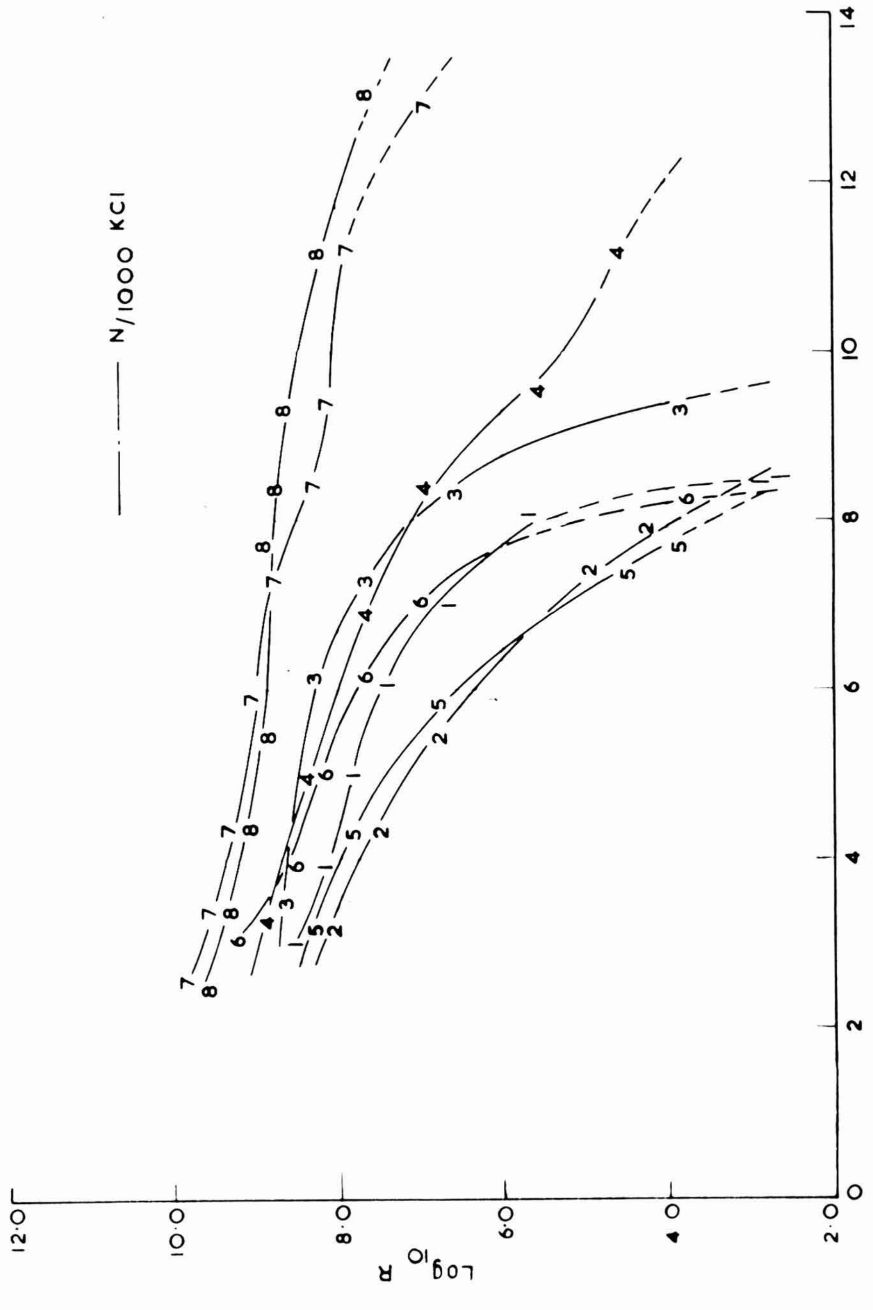


Fig. 2. Resistance of varnish films after treatment in solutions at various pH values for 5hr at 60°C

were either identical, within experimental error, or slightly lower. The breakdown in resistance of samples 1, 2, 5 and 6 in alkaline solution was particularly marked. Oleoresinous films were softened and disintegrated beyond pH 7.5. Alkyd films (samples 2 and 5) were also irretrievably damaged at pH 7.5 and completely disintegrated at pH 9.25.

Styrenated alkyd films were difficult to handle because of brittleness but otherwise showed similar behaviour to samples 2 and 5, except for a slightly enhanced resistance at all pH values.

The polyurethane and epoxy-polyamide films show a marked retention of resistance, even at high pH, although there was some fall of resistance at the highest pH values over a longer exposure time. Again it was found that results measured with 0.1N KCl were similar to, or lower than, those with 0.001N KCl. This tendency for resistance to be lower in 0.1N solution was more marked after alkaline conditioning.

Microscopic examination

Microscopic examination of the films after exposure to solutions above pH 7.5 showed disruption of the oleoresinous material (sample 6) by water droplet formation, with some linking into filiform chains of droplets. Alkyd materials (samples 2 and 5) showed similar droplets, of uniform size, less than 1.0μm diameter. This absorption of water to the extent of actual droplet formation causes the well known milky bloom of alkyd films in moist conditions. Patchiness of droplet formation was a noticeable feature, some areas being almost clear. There was no detectable droplet formation with either phenolic alkyd or epoxy ester media; nor could moisture droplet formation or apparent disruption within epoxy-polyamide and polyurethane films be detected at magnifications up to ×650. Loss of surface gloss was just perceptible after exposure to strongly alkaline conditions but alkyd films after similar treatment had almost completely disintegrated.

Variability of film behaviour

Fig. 3 shows a set of resistance measurements for linseed pentaerythritol alkyd (sample 5) films of 50μm wet-film thickness (30 to 35 μm dry).

Reproducibility was fair for most films but some anomalously high and low results were obtained. Furthermore, whilst resistance in 0.1N KCl was similar to and slightly lower than that in 0.001N KCl for the majority of films, it was significantly higher in 0.1N KCl for high resistance film and much lower in 0.1N KCl for low resistance film.

Effect of film thickness

The results shown in Fig. 4 were obtained using the same varnish but with films of 100μm wet-film thickness. In this test, four samples showed "typical" alkyd behaviour. Two samples had significantly higher resistance, although they followed the general pattern of resistance declining with increasing pH, a trend which was particularly marked beyond pH 7-8. The variation in dry-film thickness (between 62 and 69 μm) did not account for the variation in resistance and,

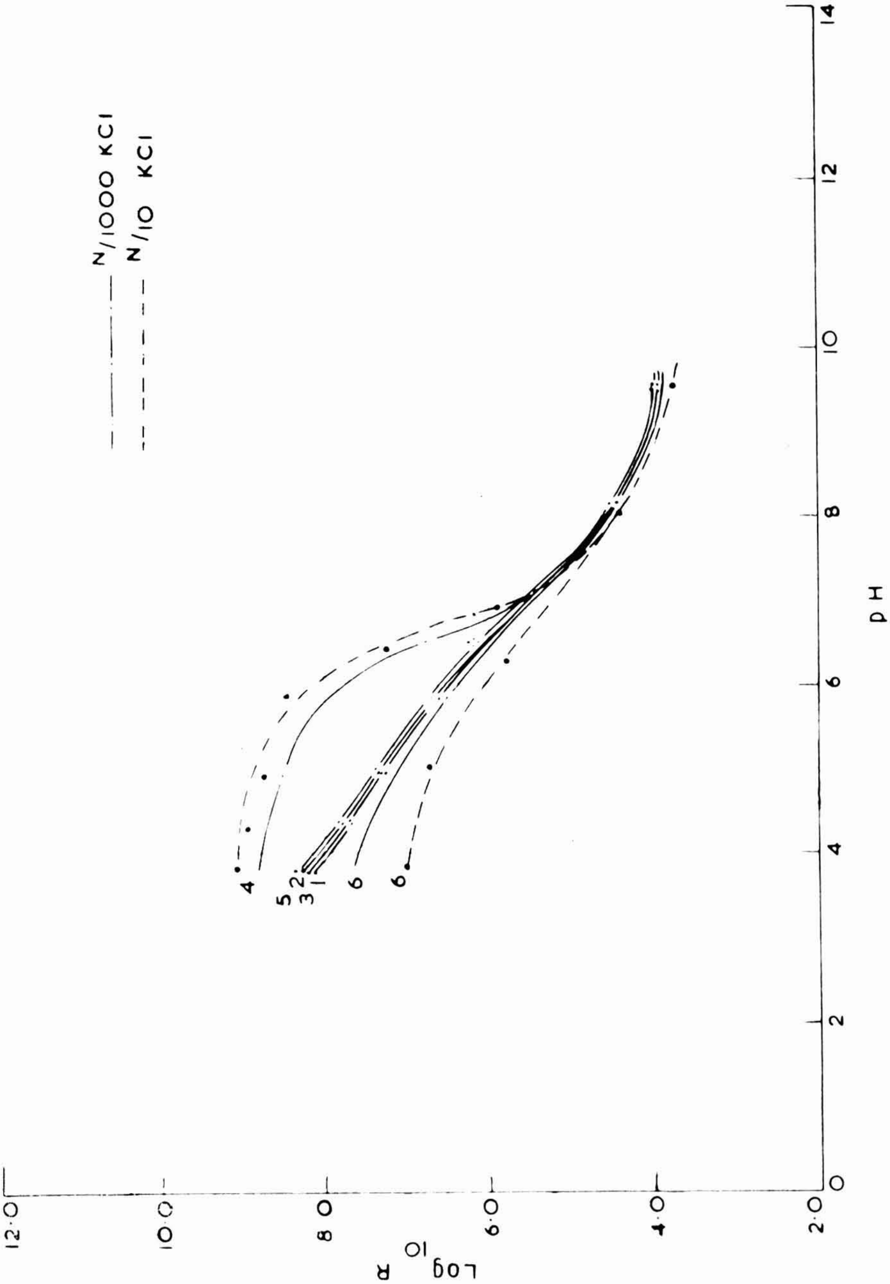


Fig. 3. Variability of resistance measurements on alkyd films (sample 5) treated at various pH values

on comparing with Fig. 2, the resistance change with pH value did not appear to be related to film thickness in any simple manner. On examining the films microscopically after conditioning, it was noted that droplet formation in the high resistance films 2 and 6 was not so marked as in the four otherwise identical films.

Comparing Figs. 3 and 4, it may be seen that the difference between the two sets of typical $\log_{10}R$ curves in the ordinate direction, between pH 4.0 and 7.5, is about 0.5. This indicates that the 62 to 69 μm thick films had a resistance approximately three times that of the 30 to 35 μm films.

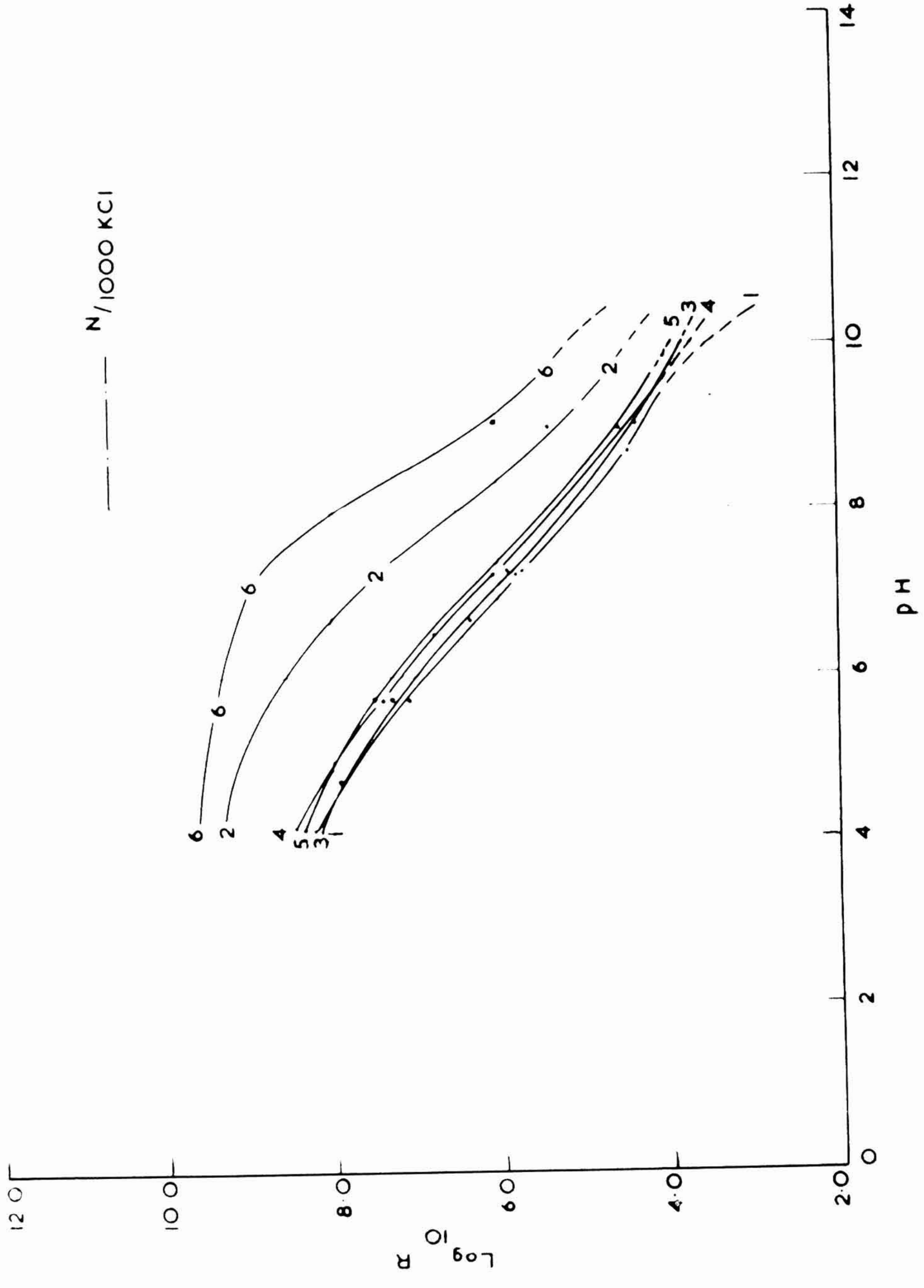


Fig. 4. Variability of resistance measurements on thick alkyd films (sample 5) treated at various pH values

Effect of concentration of electrolyte

The effect of concentration of electrolyte is shown in Fig. 5. In these tests the resistance in strong KCl was generally lower than in less concentrated solution.

The resistance values for epoxy-polyamide and polyurethane films were reproducible on returning from solutions of high to those of low concentration.

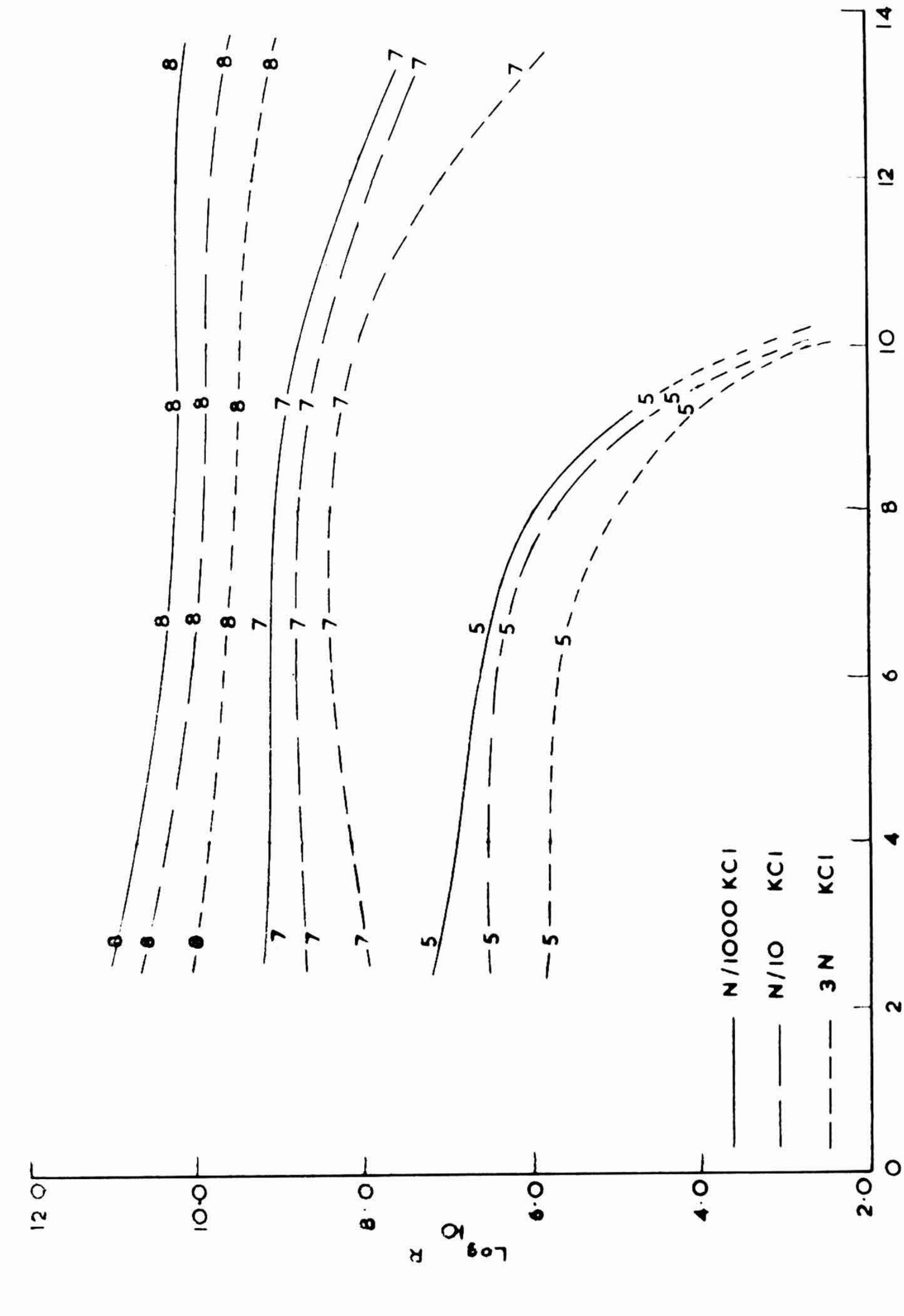


Fig. 5. Effect of electrolyte concentration on resistance of films conditioned at various pH values

Table 1

Comparison of resistance and ^{42}K cation permeation

Film	Average thickness (micro-metres)	Conditioning—pH 2.75			Conditioning—pH 8.19		
		$\log_{10}R$ ohm at 25°C	Permeation rate at 25°C after 18hr (gms ^{42}K cm^{-2} $sec^{-1} \times 10^{10}$)	^{42}K in conditioned films (counts min^{-1})	$\log_{10}R$ ohm at 25°C	Permeation rate at 25°C after 18hr (gms ^{42}K cm^{-2} $sec^{-1} \times 10^{10}$)	^{42}K in conditioned films (counts min^{-1})
Pentaerythritol alkyd ..	26	8.46	Not measureable	Not significant	6.27	4.76	420
Polyurethane	38	11.75	Not measureable	Not significant	11.30	Not measureable	Not significant
Epoxy-polyamide ..	32	7.49	Not measureable	Not significant	7.74	Not measureable	Not significant

Autoradiographs

Typical autoradiographs are shown in Figs. 6 to 9. Sets 1a and 1b show film specimens removed from test cells filled with 0.001N ^{42}KCl and 0.1N ^{42}KCl respectively. The lack of absorption of ^{42}K cations by epoxy-polyamide and polyurethane films in either acid or alkaline conditions was very striking. On the other hand the pentaerythritol alkyd showed marked absorption of cations at pH 7.73 and pH 11.42 but not at pH 3.30. Absorption was greater in 0.1N solution, as would be expected, but absorption was very uneven in most instances. The differences are much more obvious in the original films than in the illustrations, which are copies presented in reverse contrast.

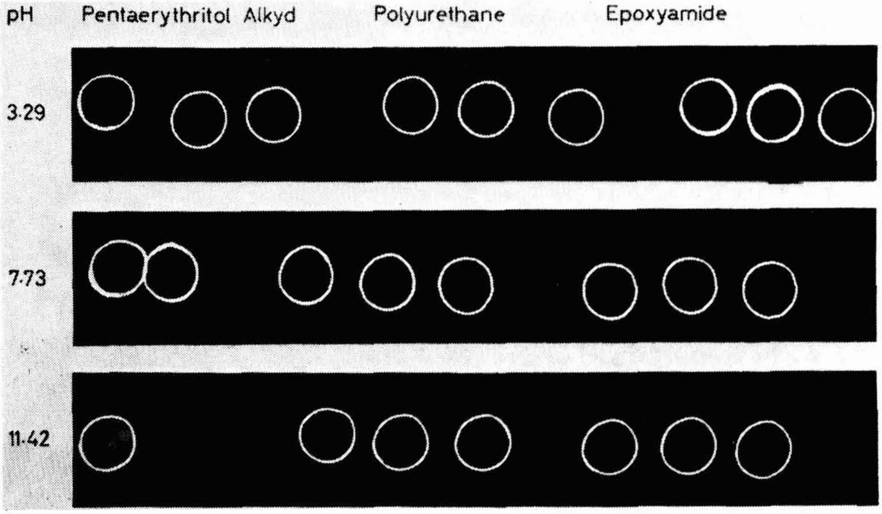


Fig. 6. Autoradiographs 1a. Film discs after permeability experiments with N/1000 ^{42}KCl at 25°C

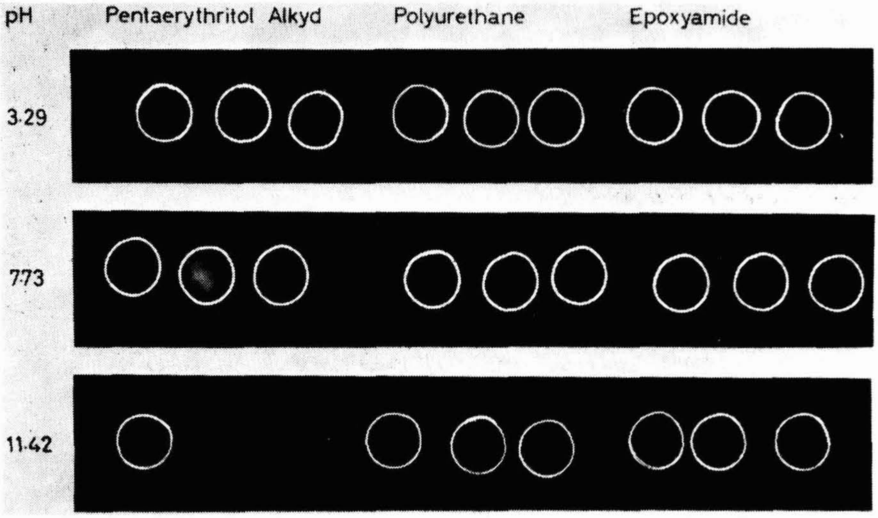
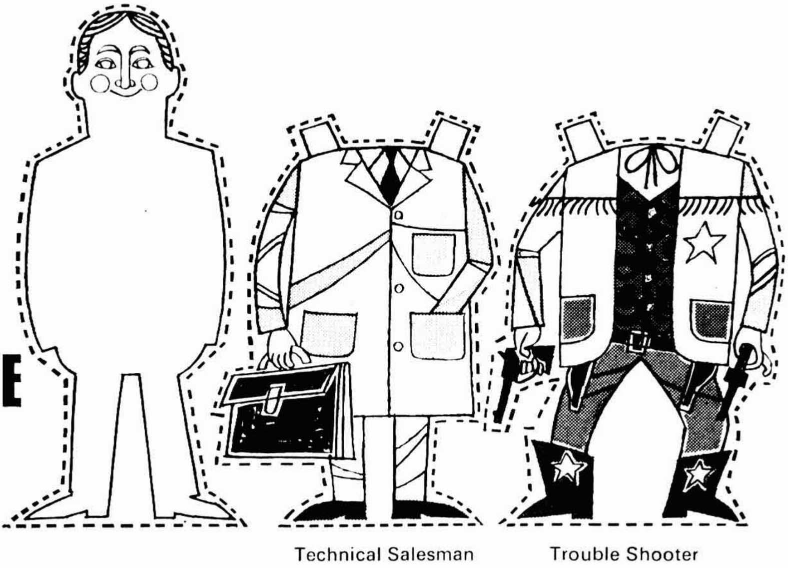
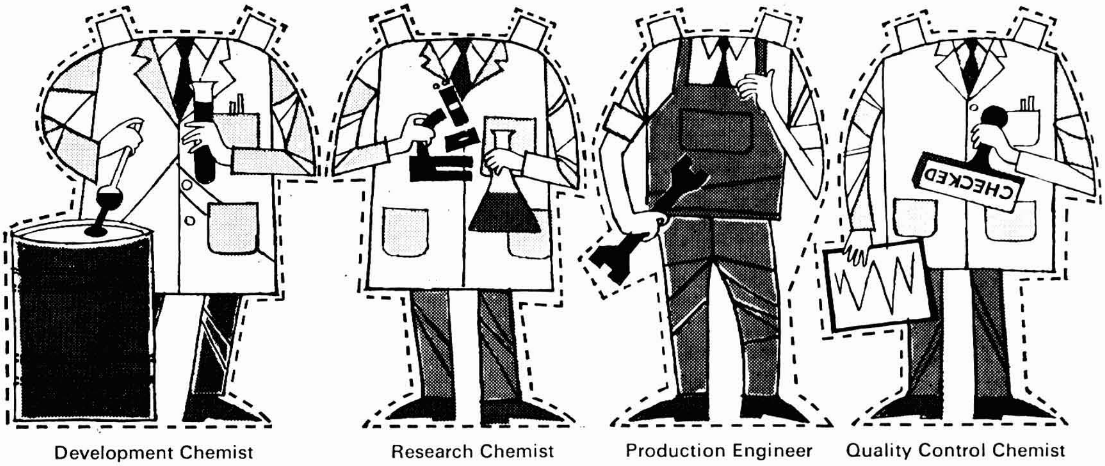


Fig. 7. Autoradiographs 1b. Film discs after permeability experiments with N/10 ^{42}KCl at 25°C


Technical Salesman
Trouble Shooter


CHECKED
Development Chemist
Research Chemist
Production Engineer
Quality Control Chemist

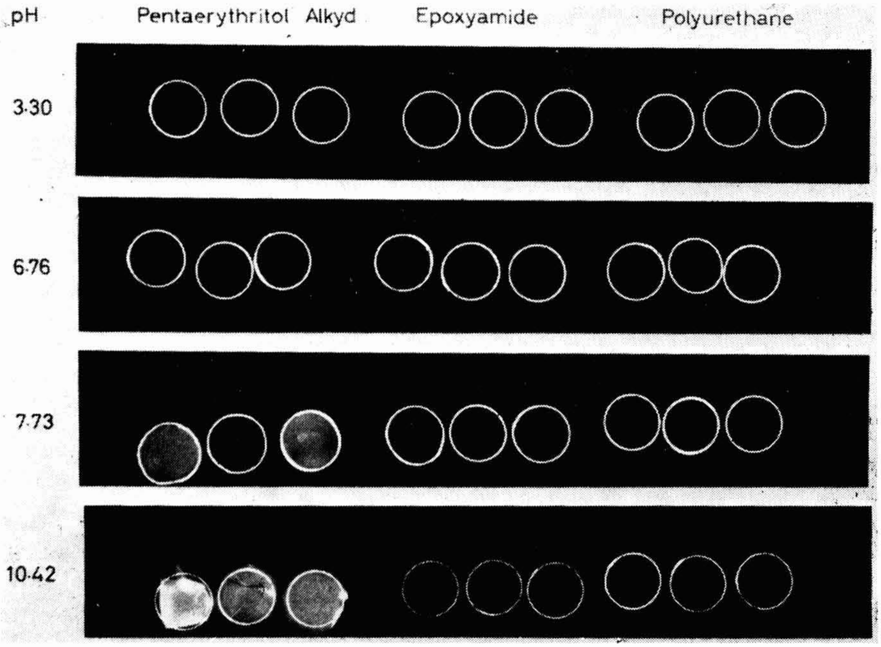


Fig. 8. Autoradiographs 2a. Film discs after conditioning in buffer solutions with ^{42}K cation for 24 hours at 25°C

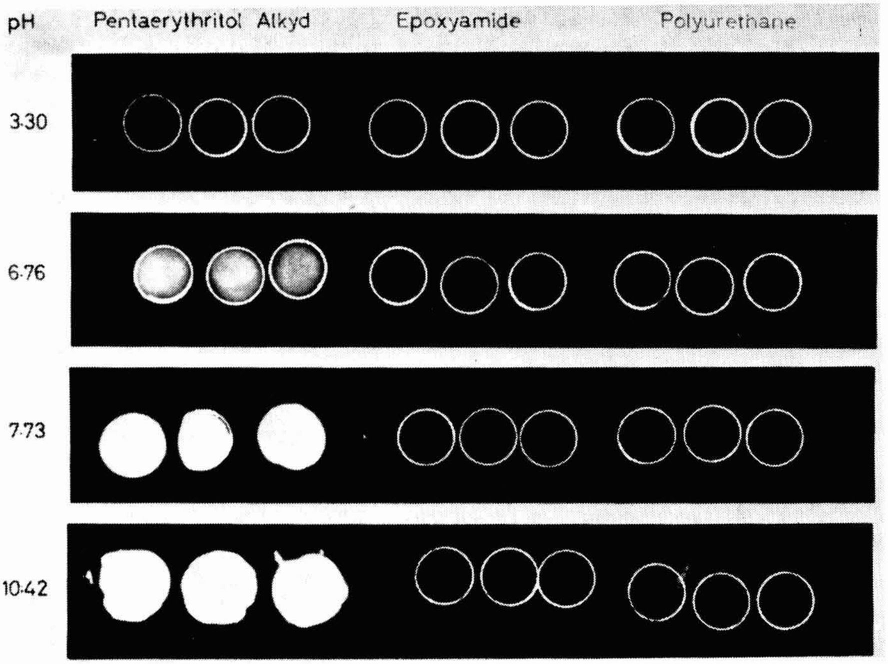


Fig. 9. Autoradiographs 2b. Film discs after conditioning in buffer solutions with ^{42}K cation for 6 hours at 60°C

Sets 2a and 2b were typical of absorption of ^{42}K cation during buffer-conditioning. Again, epoxy-polyamide and polyurethane showed negligible absorption, while that of the alkyd film was dependent upon pH.

The differences between sets 2a and 2b emphasised that, even for the alkyd resin, cation absorption at room temperature was a slow process which was by no means complete even after 24 hr. At 60°C, on the other hand, absorption was virtually complete within 5 hr. Likewise, in acid conditions, little further resistance change could be detected beyond 6 hr at 60°C. It was clear, however, that resistance changes could occur right up to the time of complete failure if the resin was disrupted by alkali. There was some indication from resistance and cation absorption measurements that disruption of alkyd material could occur on the acid side of pH 7.0 if cation absorption occurred. The virtual absence of tracer evidence in the autoradiographs of urethane and epoxyamide films suggested that either they did not undergo ion exchange or else it was an extremely slow process; this was confirmed by both resistance and radiotracer permeability measurements.

Cation permeability measurements

The comparison between resistance and permeability counts using 0.001N ^{42}KCl is shown in Table 1.

Similar results have been obtained with 0.1N ^{42}KCl. The significant count level was taken to be about 20 counts min^{-1}. ^{42}KCl has a half life of 12.45 hr and the usable period for this tracer was only about four days. Detection sensitivity declines with radioactivity decay and calculation shows that, after 18 hr, permeation of 1ng ^{42}K would still be detectable. On this basis, 53 per cent of the added ^{42}K cation had permeated the pH 8.19 conditioned pentaerythritol alkyd film in 18 hr. If diffusion or permeation was rapid, ^{42}K concentrations of the order of 5 pg would be detectable in the early stages of the experiment.

Discussion

Practical aspect

This paper deals with results obtained from accelerated tests carried out at elevated temperatures (60°C) which exaggerate the rate of attack on susceptible materials. Nevertheless, in some industrial applications such tests could be directly relevant.

Theoretical interpretation

Earlier work: The work reported here was prompted by studies made by Mayne and his colleagues[11, 12, 13] into the electrolytic resistance of polymer films. They found that the variation in resistance of detached pentaerythritol alkyd varnish films, when immersed in solutions of different pH value or cation concentration, could be characterised in terms of a "fast change" and a "slow change."

The "fast change" was reversible and was complete in less than ten minutes at 25°C. When films had been previously conditioned by prolonged exposure to buffers in which the ratio of potassium to hydrogen was low, their resistance was high in the more concentrated KCl solution and was, in fact, directly proportional to the concentration. On the other hand, when films had been conditioned in solutions in which the ratio of potassium to hydrogen ions exceeded a critical value (pH 6.5-8.0), depending on the individual film, then the "fast change" reversed and their resistance followed that of the solution, i.e. it decreased with increasing salt concentration.

This reversal was ascribed to a change in the mode of conduction of ions through the film. It was suggested that in the former case conduction was by "activated diffusion." Ions which were produced from carboxyl groups by an increase in dielectric constant in their vicinity, resulting from the presence of local accretions of water, were forced to surmount potential energy barriers in passing from one oppositely charged group to the next through an intervening area of low dielectric constant.

After reversal, on the other hand, conduction was by aqueous conduction through "virtual" pores which had been formed by the distortion of the structure of the films when small hydrogen ions were replaced by larger potassium ions.

The "slow change" was also reversible, was complete in three hr at 65°C but took three weeks at room temperature and was dependent upon the pH of the solution and the concentration of certain cations.

This change was associated with an ion-exchange process in which cations from the solution were exchanged with hydrogen ions from the COOH groups in the varnish film. The "slow change" only ceased to be reversible if the film was exposed to a solution of pH more than one unit greater than its point of "reversal"; under these conditions, degradation of the film occurred as shown by its increase in opacity and drastic fall in resistance when replaced in an acid buffer solution.

Present investigation: 1. *Variability between films*: Although this aspect is not emphasised in the papers of Mayne *et al.*, their results indicate wide variations in the resistance of nominally identical films under identical conditions of treatment. The patterns of change under varying conditions were consistent, however, and much of the work was based on the behaviour of individual films. This type of behaviour is fully confirmed by the present investigation.

2. *Shape of pH/resistance curve:* The decline in resistance of alkyd films on exposure to solutions of increasing pH value reported by Mayne is confirmed but not the increase in resistance between pH 1 and pH 8 of epoxy-polyamide film reported by Cherry and Mayne[13]. It is possible that the much shorter times of air-drying and oven-curing used in the present work or alternatively the higher epoxy resin : polyamide ratio may have some bearing on this discrepancy.

3. *Reversibility:* The reversibility of the "fast change" is confirmed but not that of the "slow change." Degradation appears to have set in at an earlier stage in the present study; this again may be due to the shorter times of drying and curing employed here, and the correspondingly lower degree of cross-linking.

4. *Direction of "fast change"*: In the present investigation, most films at all pH values were found to behave in the manner reported by Mayne *et al.* as being typical of films beyond their reversal point. The only exception was an alkyd film of unusually high resistance whose behaviour is shown in Fig. 3. Again, the only explanation which can be tentatively offered is the difference

in drying and curing conditions employed and also, possibly, the shorter time of conditioning of the films in 0.001N HCl prior to resistance measurements. Maitland and Mayne[11] reported the profound effect on their resistance of the time of immersion of alkyd films in 0.001N HCl at 60°C. This was thought to be due to the presence in varying proportion of short chain organic acids formed during the drying process.

The pronounced effects of varying the conditions of film preparation are emphasised by the difference in behaviour pattern noted above.

5. "*Slow change*"

The postulate that the decrease in resistance of alkyd films on exposure to increasingly alkaline solutions is due to a cation exchange reaction is confirmed by the radiotracer experiments; the autoradiographs offer particularly convincing evidence.

Later work: Since completion of the work described here, further evidence of the increase in ion exchange capacity, and rates of cation absorption, of alkyd films conditioned in solutions of differing pH, has been given by Ulvarsson, Khullar and Wåhlin[23]. The results for 0.1N KCl solution are especially interesting. They give some indication of a significant increase at about pH 7.0, in accord with results given here for the alkyd film.

Conclusions

This investigation has confirmed the vulnerability of alkyd and oleoresinous coating media to even mildly alkaline conditions. In marked contrast, the resistance of epoxy-polyamide and polyurethane films remained high, even after exposure to strongly alkaline solution. Their low cation absorptivity under such conditions has been demonstrated also by radiotracer measurements.

Film resistance measurements, supplemented by radiotracer studies, appear to offer a promising method of evaluating the behaviour of protective coatings towards specific chemical agents.

Correlation with conventional testing is required before the method can be used in overall durability assessment.

Acknowledgments

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The migration of lead from paint films in the rat gastro-intestinal tract

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Summary

The migration of lead from two paint films during their passage through the rat gastro-intestinal tract has been investigated. Both paints contained 2 per cent lead on the dried film, one as lead naphthenate and the other as lead chromate. Diets containing 1 per cent of the dried films were administered to groups of rats for a 12 week period; other groups received diets containing 100 ppm lead as lead naphthenate, and 20, 50 and 100 ppm lead as lead nitrate. All groups of rats remained in good health. Lead determinations were made at intervals on samples of bone, blood, kidney, liver, bile and urine. From a comparison of the analytical results it has been deduced that about one-half of the lead in the lead naphthenate paint, and about one-quarter in the lead chromate paint, migrates from the film under the experimental conditions. It is concluded that the present regulations controlling the lead content of paints intended for surfaces accessible to children are adequate to prevent future cases of lead poisoning from the ingestion of paint film.

Key words

Types and classes of coating
alkyd coating

Paint additives—driers
cobalt drier
lead naphthenate

Prime pigments
chrome orange

Properties primarily associated with materials in general
toxicity

La migration de plomb à partir des feuils de peinture dans le canal gastro-intestinal de rat

Résumé

On a étudié la migration de plomb à partir de deux feuils de peinture pendant leur passage à travers le canal gastro-intestinal de rat. Les deux peintures contiennent 2 pour cent de plomb dans le feuil sec, l'une sous forme de naphténate de plomb et l'autre comme chromate de plomb. Des régimes contenant 1 pour cent de feuils secs étaient données aux groupes de rats pendant une période de 12 semaines, d'autres groupes recevaient des régimes contenant 100 parties pour million de plomb comme naphténate de plomb, et de 20, 50, et 100 parties pour million de plomb comme nitrate de plomb. Tous les groupes de rats restaient en bonne santé. On a déterminé, par intervalles, la teneur en plomb aux échantillons d'os, sang, rein, foie, bile et urine. Par considération des résultats analytiques, on a déduit qu'un peu près de la moitié de plomb dans la peinture à naphténate de plomb, et un peu près du quart de plomb dans la peinture à chromate de plomb, doivent migrater sous les conditions expérimentales. On conclut que les règlements gouvernant la teneur en plomb des peintures destinées aux surfaces accesibles aux enfants sont suffisants pour éviter à l'avenir des cas d'intoxication par le plomb lors de l'ingestion des feuils de peinture.

Das Wandern von Blei aus Anstrichfilmen in den Magen-Darmkanal von Ratten

Zusammenfassung

Die Migration von Blei aus zwei Anstrichfilmen während seines Durchganges durch den Magen-Darmkanal von Ratten wurde untersucht. Beide Farben enthielten 2 Prozent Blei (Trockengewicht), die eine als Bleinaphthenat und die andere als Bleichromat. Während zwölfwöchigen Perioden wurden Gruppen von Ratten mit 1 Prozent des Trockenfilms enthaltenden Diäten gefüttert; andere Gruppen erhielten Diäten mit 100 Teilen p.m. Blei als Naphthenat und 20, 50 und 100 Teilen p.m. Blei als Nitrat. Alle Rattengruppen blieben gesund. Bleibestimmungen wurden in Zwischenräumen an Proben von Knochen, Blut, Niere, Leber, Galle und Urin vorgenommen. Aus Vergleichen der analytischen Resultate wurde geschlossen, dass etwa die Hälfte des Bleies in der Bleinaphthenatfarbe und etwa ein Viertel in der Bleichromatfarbe unter den experimentellen Bedingungen aus dem Film wandert. Es wird gefolgert, dass die bestehenden Bestimmungen für die Kontrolle des Bleigehaltes von Farben, die für Kindern zugänglichen Oberflächen vorgesehen sind, genügen, um in Zukunft Fälle von Bleivergiftung durch Ingestion von Farbfilm zu verhüten.

Миграция свинца красочных пленок в желудочно-кишечном тракте крыс

Резюме

Исследовалась миграция свинца двух красочных пленок при их проходе через желудочно-кишечный тракт крыс. Обе краски содержали 2 процента свинца в сухой пленке, одна в виде нафтеновосвинцовистой соли а другая в виде хромовокислого свинца. Диета содержащая 1 процент этих сухих пленок давалась группам крыс в течение 12-ти недель; другие группы крыс получали диету содержащую 100 частей на миллион свинца в виде нафтеносвинцовистой соли и 20, 50 и 100 частей на миллион свинца в виде азотносвинцовистой соли. Все группы крыс остались здоровыми. Определение свинца производилось через промежутки времени в образцах кости, крови, почек, печени, желчи и мочи. Сравнение аналитических результатов показало что около половины свинца в краске содержащей нафтеносвинцовистую соль и около четверти свинца в краске содержащей хромовокислый свинец, мигрирует из пленки при условиях оныта. Делается заключение что существующие требования контролирующие содержание свинца в красках предназначаемых для поверхностей доступных для детей, являются достаточными для предотвращения в будущем случаев отравления свинцом путем глотания красочной пленки.

Introduction

Since the turn of the century, there has been a progressive decrease in the incidence of occupational lead poisoning. In 1930 there were 32 fatal cases notified to the Factory Department, but none was reported over the period 1957-1966. Non-fatal cases fell from 233 in 1930 to 80 in 1966. These improvements have been in part due to the enforcement of regulations under the Factories Acts, and in part to advances in education and in the dissemination of information, and to a greater attention to occupational health.

Only a small proportion of the reported cases are attributable to the application of lead-containing paints. There have, however, been numerous cases of non-occupational lead poisoning, mainly in children, which are thought to derive from the ingestion of flakes of dried lead paints detached from treated woodwork. In Chicago alone, over the period 1959-1961, 429 such cases were recorded, of which 67 were fatal[3]. Other cases have been reported by Chisholm & Harrison[2] and by Moncrieff *et al*[7]. This high incidence of poisoning may be due to the high lead content of paints formerly used for interior decoration and to the friable nature of old paint films, which renders possible their disintegration into small particles with a large surface area when chewed and swallowed. It has also been suggested that young children are more sensitive to lead than are adults[5].

With the object of protecting children the paint industry gave a voluntary undertaking to the Ministry of Health in 1963 that paint containing more than 1 per cent lead on the dried film should bear a warning label indicating that the colour should not be applied to toys, furniture or interior surfaces which might be chewed by children. Subsequently the labelling of surface coatings intended for toys was controlled by the Toys (Safety) Regulations 1967 which limited the lead content of the film to 1.1 per cent, reducing to 0.5 per cent in 1968.

In a previous publication[4], the migration of lead from polymers in the gastro-intestinal tract has been studied by incorporating the ground polymer into the diet of rats and then measuring lead in tissues and excreta, and comparing the results with those of similar experiments in which a lead salt was incorporated in the diet. By comparing the amounts of lead absorbed in these two sets of experiments, it was possible to relate the diets containing the polymers to the diets containing lead salt, and hence to estimate the extent to which lead migrated from the polymer into the gut contents. It was concluded from these experiments that the difficulty in masticating these materials prevented any risk of lead poisoning from their ingestion. This limitation evidently does not apply to paint film, so the investigation has been extended to ascertain the extent to which lead can be mobilised from a paint film, and to confirm that the present regulations provide an adequate protection. Two paints have been included in the investigation; one containing lead as a drier and the other a lead pigment.

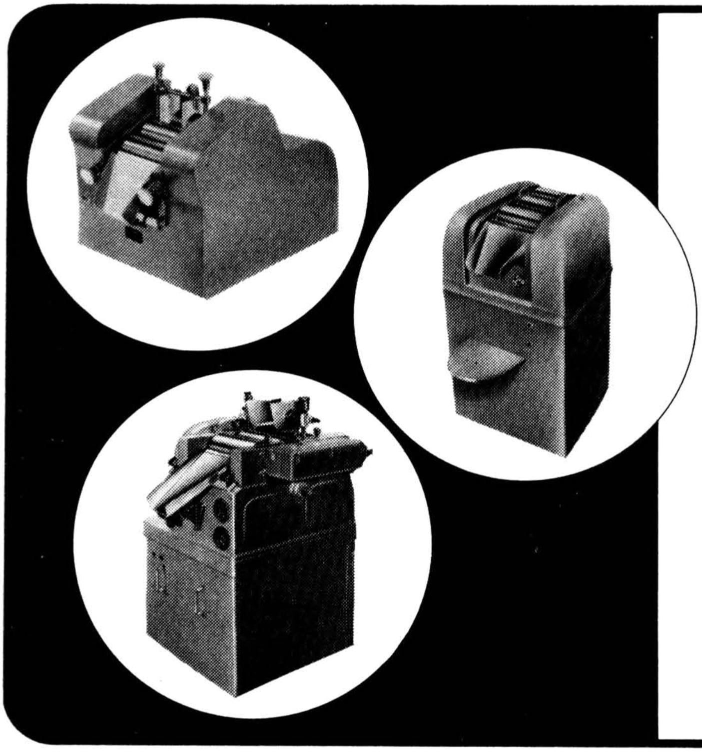
Experimental

Materials investigated

The paint used in this investigation was an off-white gloss finish based on an oil-modified alkyd resin. It contained cobalt drier without lead. To one portion was added Middle Orange Chrome pigment to produce approximately 2 per cent lead in the dried film, and to another portion was added lead naphthenate drier to produce approximately the same final lead content.

Preparation of diets

The paints were brushed on to pieces of tared rice paper, 75 × 50cm, and allowed to dry for three days. After reweighing to assess the weight of the paint film, the sheets were placed in an oven at 90°C for three hours to render them brittle. Unpainted rice paper was similarly dried for use in the control diet. The painted and control rice papers were broken up and homogenised in a small volume of water and the resulting slurry mixed with malt extract and corn oil and then incorporated into the standard rat diet[1] to give a final concentration of 1 per cent paint film in the pellets. The rice paper content of the diet was about 0.5 per cent, and the same amount was added to the control diet. The diets based on the lead chromate and lead naphthenate films were found by the analytical method described below to contain 192 and 190 ppm lead respectively. For the diets containing lead nitrate the salt was added in aqueous solution; lead naphthenate was dissolved in the corn oil. The control diet was found by the method described below to contain 1.3ppm lead.



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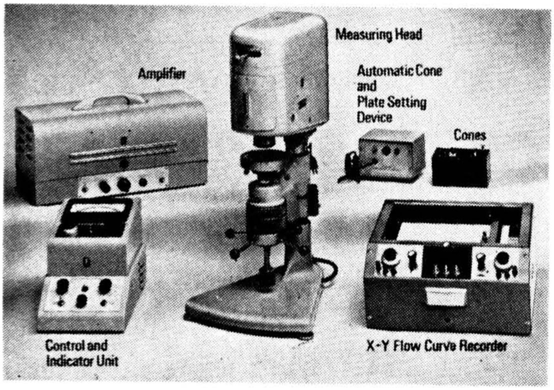

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Animal experiments

The animal experiments were performed as previously described[4]. The diets were administered to groups of 30 young male albino rats for a 12 week period. At intervals animals were killed and samples of bone, blood, kidney and liver were taken for lead determinations. Analyses of bile and urine were made at 4 and 12 weeks; earlier experiments with rats receiving lead salt diets had shown that no appreciable amounts of lead were excreted in bile earlier than 4 weeks.

The weight of the rats was measured at weekly intervals throughout the experiment and the food intakes were recorded. At the end of the feeding period blood samples were examined for haemoglobin content, packed cell volume, white and differential cell counts, platelet count, and for the presence of stippled cells and reticulocytes. Bone marrow was examined for punctate basophilia and for immature red cells.

The determination of lead

The determination of lead in liver, kidney, bone, bile and urine was made by the methods previously described[4]. Increased sensitivity in the method for blood was achieved by carefully evaporating a 5ml sample to dryness with 2ml nitric acid and ashing the residue at 500°C. The ash was dissolved in 5ml water and 10ml 5N hydrochloric acid and the lead was determined by the colorimetric method. The experimental diets were ashed by the method used for bone and the residue was dissolved in 0.5ml hydrochloric acid and 0.25ml nitric acid and diluted to 10ml with water. The solution was polarographed with a Cambridge Pen-writing Polarograph and Univector over the range -0.2 to -0.8 v, and the peak heights obtained were compared with those of standard lead solutions.

Results

The concentrations of lead found in the tissues, bile and urine of the test and control rats throughout the experimental period are shown in Tables 1-6. In all experiments the rats remained in good condition and no significant difference was observed between the growth and food intake of test and control animals. No changes were observed in blood or bone marrow, indicative of early stages of lead poisoning.

The absorption of lead from lead salt diets

Lead nitrate: Table 4 shows little difference between the urinary excretion of lead by control animals, and by those receiving the lead nitrate diets, even at the highest concentration. These results confirm an earlier observation that urinary excretion in the rat cannot be used as an index of lead released into the gut[4].

The concentration of lead in bone, kidney and liver tissue increased with the dose. With kidneys and liver a rise is apparent within the first two weeks and the concentration remains fairly constant throughout the 12 week experiment. The accumulation in bone is slower and the concentration appears to reach an approximately constant value at about 8 weeks. The concentration of lead in the blood (Table 5) shows some correlation with the dietary concentra-

Table 1
Lead content of bone (femur)

Diet	Weeks				
	0	2	4	8	12
Control	1.08 (10)	0.53 (4)	0.93 (4)	0.94 (4)	0.73 (4)
Lead nitrate					
as Pb 20ppm		0.90 (2)	1.36 (2)	3.31 (2)	1.67 (2)
50ppm		2.14 (2)	3.00 (2)	5.11 (2)	3.74 (2)
100ppm		4.41 (2)	6.90 (2)	5.72 (2)	7.34 (2)
Lead naphthenate					
as Pb 100ppm		3.11 (2)	6.03 (2)	6.17 (2)	6.20 (4)
Lead paints					
Chrome pigment		2.46 (2)	1.52 (2)	5.20 (2)	4.61 (2)
Naphthenate		4.34 (2)	2.15 (2)	9.23 (2)	7.57 (2)

Analytical results are expressed as μg/g wet weight, and are the means of determinations on the number of animals indicated in parentheses.

Table 2
Lead content of kidneys

Diet	Weeks				
	0	2	4	8	12
Control	0.45 (10)	0.24 (4)	0.40 (4)	0.27 (4)	0.22 (3)
Lead nitrate					
as Pb 20ppm		0.54 (2)	0.70 (2)	0.67 (2)	0.79 (2)
50ppm		0.99 (2)	1.38 (2)	1.25 (2)	1.16 (2)
100ppm		1.53 (2)	2.25 (2)	1.86 (2)	1.59 (2)
Lead naphthenate					
as Pb 100ppm		1.66 (2)	1.78 (2)	1.60 (2)	1.83 (2)
Lead paints					
Chrome pigment		1.00 (2)	0.99 (2)	1.05 (2)	0.98 (2)
Naphthenate		1.12 (2)	1.78 (2)	2.11 (2)	2.07 (2)

Analytical results are expressed as μg/g wet weight, and are the means of determinations on the number of animals indicated in parentheses.

Table 3
Lead content of liver

Diet	Weeks				
	0	2	4	8	12
Control	0.08 (5)	0.12 (4)	0.12 (4)	0.12 (4)	0.14 (2)
Lead nitrate					
as Pb 20ppm		0.21 (2)	0.19 (2)	0.22 (2)	0.28 (2)
50ppm		0.23 (2)	0.28 (2)	0.30 (2)	0.29 (2)
100ppm		0.35 (2)	0.30 (2)	0.37 (2)	0.31 (2)
Lead naphthenate					
as Pb 100ppm		0.28 (2)	0.28 (2)	0.24 (2)	0.31 (2)
Lead paints					
Chrome pigment		0.17 (2)	0.18 (2)	0.19 (2)	0.23 (2)
Naphthenate		0.23 (2)	0.33 (2)	0.30 (2)	0.32 (1)

Analytical results are expressed as μg/g wet weight, and are the means of determinations on the number of animals indicated in parentheses.

Table 4
Lead content of urine

Week	Control	Lead salt diets (as Pb)				Paint diets	
		Lead nitrate			Lead naphthenate	Chrome pigment	Naphthenate
		20ppm	50ppm	100ppm	100ppm		
4	0.96 (26) 0.72 (17) 0.73 (20) 1.23 (19)	0.86 (22) 0.64 (8)	1.01 (18) 0.93 (17)	1.38 (18) 0.79 (13)	1.36 (30) 0.92 (14)	1.22 (30) 2.15 (23)	0.61 (23) 0.96 (10)
12	0.67 (12) 0.98 (12) 0.96 (32) 1.04 (24)	1.07 (32) 1.20 (30)	1.17 (16) 1.30 (21)	1.79 (24) 1.37 (25)	1.37 (31) 1.35 (26)	1.66 (19) 0.90 (24)	1.00 (16) 1.18 (27)

Results are expressed as μg/rat/24hr, and each is based on the pooled 24-hr urine from a group of five rats. Figures in parentheses, urine volume (ml/rat/24hr).

Table 5
Lead content of blood

Diet	Weeks				
	0	2	4	8	12
Control	0.12 (10)	0.07 (4)	0.04 (4)	0.07 (4)	0.11
Lead nitrate					
as Pb 20ppm		0.09 (2)	0.08 (2)	0.12 (2)	0.16 (2)
as Pb 50ppm		0.11 (2)	0.11 (2)	0.12 (2)	0.24 (2)
as Pb 100ppm		0.14 (2)	0.31 (2)	0.15 (2)	0.24 (2)
Lead naphthenate					
as Pb 100ppm		0.15 (2)	0.36 (2)	0.14 (2)	0.16 (2)
Lead paints					
Chrome pigment		0.10 (2)	0.06 (2)	0.06 (2)	0.13 (2)
Naphthenate		0.19 (2)	0.13 (2)	0.10 (2)	0.19 (2)

Results are expressed as μg/ml, and are the means of determinations on the number of animals indicated in parentheses.

Table 6
Lead content of bile

Week	Control	Lead salt diets (as Pb)				Paint diets	
		Lead nitrate			Lead naphthenate		
		20ppm	50ppm	100ppm	100ppm	Chrome pigment	Naphthenate
4	0.016 (16) 0.012 (15)	0.03 (6) 0.022 (15)	0.033 (15) 0.026 (10)	0.146 (19) 0.274 (12.5)	0.103 (20) 0.119 (20)	0.082 (12.5) 0.053 (20)	0.140 (17) 0.130 (16)
12	0.038 (12.5) 0.049 (19)	0.100 (11) 0.100 (18)	0.095 (11) 0.096 (12.5)	0.159 (13) 0.126 (14)	0.114 (17.5) 0.116 (20)	0.071 (17.5)	0.117 (10) 0.135 (13.5)

Results are expressed as μg/ml. Each determination was made on a separate rat. Figures in parentheses indicate volume of bile collected (ml/rat/24hr).

tion, but this is not so marked as it is in other tissues. Bile provides a sensitive index of lead absorption, though the correlation with dietary concentration is somewhat erratic (Table 6).

Lead naphthenate: The concentration of lead in the tissues, urine and bile of rats receiving the lead naphthenate diet is similar to that observed after the administration of a diet containing an equivalent amount of lead nitrate. The acid radical does not, therefore, affect the availability of the lead.

The absorption of lead from paint films

Chrome pigment: The concentration of lead increases in kidneys and bone during the first two weeks; in the former tissue it thereafter remains fairly constant throughout the experiment, and with the latter the concentration continues to rise until the eighth week. There is a slight increase in the lead content of liver, but the blood concentration is not significantly different from the control value. There is an appreciable excretion of lead in the bile but the amount in urine is negligible.

The amount of lead in bone, kidney and bile of rats receiving the chrome pigment paint diet is similar to that observed in the rats on the 50ppm lead nitrate diet.

Lead naphthenate paint: The uptake of lead by kidney, bone and liver is much greater than that observed with the chrome pigment paint, and it parallels the findings in rats on the 100ppm lead nitrate diet. This conclusion is supported by the bile results and, to a smaller extent, by the blood analysis. There is again no significant increase in the lead content of urine in spite of the considerable absorption of lead demonstrated by the analytical results on tissue and bile.

Discussion and Conclusions

The work of Chisholm & Harrison[2] has shown that the daily average lead excretion in the faeces of children showing signs of lead poisoning after ingestion of paint flakes, is 44mg. As most of the lead ingested appears in faeces, it may be assumed that a daily intake of in the region of 50mg lead is very dangerous, unless the lead is in a form not available for absorption. On the other hand, Kehoe[6] has shown that a daily intake of 1mg soluble lead salt in the diet over a period of years is without risk. The present investigation has demonstrated that about one-half of the lead in the lead naphthenate paint, and one-quarter in the chrome pigment paint, can migrate from the film into the gut content, and Table 7 shows the amounts of the two paints which must be ingested daily

Table 7

Hazard from paint ingestion

Paint	Threshold (1mg dose)		Danger (50mg dose)	
	Weight, g	Area, cm²	Weight, g	Area, cm²
Chrome pigment	0.2	20	10	1,000
Lead naphthenate	0.1	10	5	500

Figures give weight and surface area (average single coat) of paint containing 2 per cent lead on dried film which, if ingested daily, would reach threshold of safety or be very dangerous.

to produce the threshold and the dangerous lead intakes. The observed migration of lead from paint film is much greater than that recorded in earlier experiments with polymers[4]; this may be due to the much finer state of subdivision attained with paint film. It is possible that the mechanical means used to disintegrate the film was much more efficient than the processes of mastication and digestion, and the migration figures achieved in these experiments may be in excess of those encountered when paint flakes are ingested.

The undertaking by the paint industry to limit the lead content of finishes for surfaces likely to be chewed by children to not more than 1 per cent is in agreement with recommendations of the British Standards Specification and the American Standards Association. The amounts of such paints which must be ingested to achieve the threshold and toxic amounts would be about double the figures in Table 7. With coatings containing not more than 0.5 per cent lead in conformity with the latest Toys (Safety) Regulations, the amounts would be about four-fold. It is certain that these figures indicate no hazard so long as the film is adherent for it would be impossible to ingest sufficient either by detaching the film manually or by gnawing it off the support. A greater lead intake would be possible if detached films were available for ingestion but, even so, with paints of this type, there seems little justification for the fears expressed by Chisholm and Harrison, that poor maintenance of modern housing with resultant accumulation of many layers of paints on surfaces accessible to children, may in the future constitute a hazard to small children.

Acknowledgments

Technical assistance in this investigation was provided by Mr P. B. Hall. We acknowledge the co-operation of Dr D. G. Clark, who provided the bile-cannulation preparations.

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Next month's issue

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

"Exterior durability of coatings," *by J. E. Fullard.*

"Epoxy resin floor finishes in South Africa," *by L. Muller.*

"Acrylic resins for industrial chemical coatings," *by H. L. Wampner.*

"The surface treatment of pigments," *by J. L. Moilliet and D. A. Plant.*

Editorial

Who said functionality?

In writing the Student Review which appears elsewhere in this issue, we were reminded of the striking dichotomy of opinion about the originator of the functionality concept. R. H. Kienle is the favourite of the coatings technologists, and one well known text book, aimed mainly at coatings students, contains a chapter headed "Kienle's functionality theory of resin formation". On the other hand, if one talks to academic polymer scientists or to specialists in rubbers, fibres or plastics, "functionality" is invariably coupled with the name of W. H. Carothers, and Kienle's contributions are unlikely to be mentioned. It is of interest, therefore, to examine the early writings of these two giants, the more so since both were propounding their ideas at the same time, that is, in the years around 1930 when Staudinger and others, who favoured the covalent macromolecule, were gaining supremacy over the micellar theorists.

In September 1928, Kienle, with C. S. Ferguson, presented a paper to the ACS (*Ind. Engg. Chem.* 1929, **21,** 349) discussing alkyd resins as film-formers, and classifying them as heat-non-convertible, heat-convertible and oxygen-convertible. He clearly recognised the value of diols (with dicarboxylic acids) in making non-convertible resins, and pointed out the need to use trihydric and higher polyhydric alcohols to achieve heat-convertibility. He referred to "lower valent alcohols and acids" as retarding gel time, reducing heat-convertibility, decreasing acid value and increasing attainable degree of esterification in alkyds, clearly demonstrating his mastery of alkyd formulating principles, but stopping just short of providing a molecular picture; and nowhere using the term "functionality."

In April 1930, Kienle presented his most famous paper, again to the ACS, in which he put forward his three postulates concerning the formation and properties of polymers (*Ind. Engg. Chem.*, 1930, **22,** 590). He acknowledged Carothers's early papers, and pointed out that the text book of Scheiber and Sänding was the only one (of three!) which then attempted to deal with the underlying causes of resin formation. Kienle here showed his favour for the macromolecular concept, but rightly observed that, whilst long chain formation was important, something more was needed to explain gelation, of glyceryl phthalate for example. The three postulates are too well known to warrant discussion; suffice it to say that they are remarkable for the insight they provided into what happens in polymerising systems. Indeed, they still summarise the picture more neatly than many a recent lengthy discourse. In this paper, Kienle went so far as to illustrate the cross-linked macromolecule (though he referred to intertwining rather than cross-linking) but, despite his awareness of Carothers's publications (*qv*), he still did not adopt the term functionality. Instead, he defined "the *reactivity* of any substance . . . as the number of primary valence bonds which are active in the reaction under consideration."

In the meantime, Carothers had distinguished between addition and condensation polymerisations, and had defined the term functionality thus: "A functional group in the monomer is such an arrangement of atoms as might lead to a reaction step. According as the monomer contains 1, 2, 3 etc., it is called monofunctional, bifunctional etc." (*J. Amer. Chem. Soc.* 1929, **51,** 2548). However, whereas Kienle was working mainly with alkyds, typically comprising triols, Carothers was concerned predominantly with bifunctional reactants. He defined the circumstances in which ring formation and linear polymer formation would be preferred, and paid little attention to gelation until 1931, when he first appears to have recognised the work of Kienle. He then stated that the difference between the glycol-phthalic and glycerol-phthalic reactions was "obvious," and explicable in terms of one-dimensional *versus* three-dimensional polymer growth. He also freely used the term "cross-linking." (*Chem. Rev.* 1931, **8,** 353). This is in sharp contrast to Kienle who five, and even eight, years later, showed a reluctance to interpret the gelation of glyceryl phthalate in terms of the infinite three-dimensional macromolecule concept, preferring his own "log-jam" theory. (*J. Soc. Chem. Ind.* 1936, **15,** 229T; *J. Amer. Chem. Soc.* 1939, **61,** 2258). Both these papers followed Carothers's highly significant contribution of a quantitative treatment of functionality, and his derivation of the well-known equation relating degree of polymerisation to degree of reaction and functionality. (*Trans. Farad. Soc.* 1936, **32,** 39). The further development of these ideas by Flory, Stockmayer and others is "modern history." Its relevance to this discussion is frankly speculative: had the distinction between number average and weight average molecular weights been appreciated earlier, it is probable that Kienle and Carothers would have been speaking a common language, each reinforcing the ideas of the other more obviously than they did in the event.

Instead, what emerges from a reading of their publications is a realisation that both Kienle and Carothers were cautious in their interpretation of their own work and in their acceptance of the postulates of others. They worked in different industries, for the most part, with different objectives and with different materials; yet independently they were formulating one of the greatest unifying theories of modern polymer science. Kienle must take credit for his far-sighted three postulates, Carothers for his quantification of functionality theory; but to assign priority for the steps between one is obliged to speculate about their thinking. Who first *said* "functionality" must remain an open question. Carothers *wrote* it before Kienle, but the idea is so clearly foreshadowed in Kienle's alkyd paper of 1928 that he may very well have been the first to *think* it.

Correspondence

Leonardo da Vinci

SIR,—Being retired (over three years now, how they have flown), I have now more time at my disposal for the leisurely pursuit of my interests. How better then than to spend some of it in a well-equipped municipal or university library and fill in some of the gaps in one's knowledge by gently browsing and following any interesting trail. There is no need for me to dwell on the restful satisfaction that comes from time spent in this way for I am sure our essayists have written at length on such delights. So I found myself one day turning over the pages of some of the many books dealing with the life and work of Leonardo da Vinci, who holds special significance for our Association.

At the 1968 AGM at Bristol, Dr Keenan gave some details of the origin of OCCA's adoption of this genius (see also G. Copping's History of the Association p. 49), and I began to wonder how many of our members knew, except in the vague way I did myself, the range of Leonardo's knowledge in such diverse fields as painting, sculpture, anatomy, architecture, mathematics, flight, engineering and various sciences. Even this list does not cover entirely the full breadth of his interests, as a glance through the two volumes of Leonardo's Notebooks will readily show.

Notwithstanding the fact that some of the branches of knowledge he gave his attention to were in their early stages of development and that his reports on some of them were fragmentary, the Notebooks provide eloquent testimony to the agility of mind of a man who sought to encompass all the knowledge of his period and present it as a unified whole. His thinking was conditioned by a strong belief in a close link between science, with its objective investigations and ordered findings, and art as a presentation and interpretation of the world he lived in.

It may be said that the creative genius of Leonardo lay in this mutual intensification of his artistic and scientific abilities. He used his skill as an artist to present his scientific observations with a clarity excelling anything possible through mere words, though his style of writing, with its extraordinary lucidity and directness, had a power which shows through translation. Critics blame Leonardo the artist for his scientific pursuits or Leonardo the scientist for the limitations ultimately inherent in the fact that his aims were artistic ones. For, primarily, Leonardo was an artist, though he planned less than fifty pictures, of which probably not more than ten of guaranteed authenticity have been preserved. (It has been said, though, that in The Last Supper, The Battle of Anghiari and the Mona Lisa he expressed, to the highest degree of perfection, everything he had to say about Man and his concerns). Small wonder perhaps when one considers his lengthy excursions into those many other fields of activity that many, if not most, of his projects were not completed and his aim to present man's total knowledge in encyclopedic form, embracing every realm of nature and the spirit, was never achieved.

Nevertheless, in all that he undertook, Leonardo was imbued with a constant desire to represent the true, the right and the beautiful as a universal harmony and that would have been the underlying theme of such a "magnum opus." Perhaps, in this fusion of knowledge, we can appreciate better the present trend in our universities to avoid sharp divisions between the different departments of study ("disciplines" as we say these days) and to make students reading the arts and sciences respectively more aware of how the others think and work.

The real purpose of this letter is to interest members in the mind and erudition of the man whose portrait has, over the last 21 years, become so familiar on the Presidential badge and the Association's literature—and even its tie!

I wonder how many members would have a ready answer if asked what Leonardo meant to the Association. Should any of them wish to read more than is to be found in an encyclopedia or other book of reference, then there is a wealth of literature about this remarkable man on whom the heavens seem to have rained down their richest gifts. Indeed, the records credit him with so many good qualities that one could be forgiven a measure of disbelief. The index in the Henry Watson Art Library in Manchester, for example, contains an inch thickness of cards on Leonardo, and other less specialised libraries can generally offer a good selection of books. After several hours' browsing I found the most readable critical account of Leonardo's work in the translation of L. H. Heydenreich's book on him and I would commend it to anyone, like myself, wanting to add to his knowledge of OCCA's adopted patron. Those interested in Leonardo's paintings and drawings would find the handsome volume by L. Goldscheider very attractive, or Sir Kenneth Clark's account, which is available also in the Penguin edition. Had I ready access to Dr Jordan's many lectures to scientific societies I should be interested to re-read those in which he treated of the skill and philosophy of the craftsmen and artists, particularly the old masters whom he so much admired, looking for any reference he will surely have made to Leonardo.

I was interested to read recently in the national press an account of the Leonardo da Vinci lecture given this year by the chief engineer of the Automobile Association in the University of Strathclyde and was curious enough to write to the University for information about the significance of Leonardo for them. I learned that this was the thirteenth annual lecture of the series and that it is sponsored by the Scottish Branch of the Institute of Mechanical Engineers. Apparently their choice of that name for these lectures was based on the pioneer engineering activities of Leonardo, testimony enough to his ability in that field.

Yours faithfully,
V. G. Jolly.

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Storth,
Milnthorpe,
Westmorland.

Reviews

PRINCIPLES OF CHEMICAL SCIENCE

By L. W. M. TYRRELL and R. K. WARREN. London: Edward Arnold (Publishers) Ltd., 1968, Pp. 272, price 42s.

So much technology, so many people to be trained, but so many branches of technology that the numbers of students are not always adequate to meet the requirements for holding specialist courses, at least not at all levels. This position is aggravated by the wide geographical distribution of some industries. In recent years there has been a trend towards basic scientific training preceding technological training, or at least successive periods of scientific and industrial training as in sandwich courses, rather than a mixed scientific/technological training from school-leaving onwards. In the paint industry the revised City and Guilds schemes include a two-tier scheme for paint technicians, the first to cover training as chemical technicians (unless there is already evidence of sound primary chemical knowledge), before proceeding to paint technology.

This book is timely, being intended (as the preface has it) "primarily for laboratory assistants or technicians in industry who are following a part-time, sandwich or block-release course of study at a college," the contents being based on the syllabuses for Chemical Technicians Certificates. Manifestly, however, it also has a wider potential audience including those involved in full time studies and non-scientists wishing to gain some knowledge of main principles. It could reasonably be added that it is also a good "refresher" course for established technicians whose immersion in their everyday technical work may have somewhat blurred memories of the basic science and its developments. Let those of us who were trained years ago not be too superior about this for there is nothing wrong in quietly admitting, if only to oneself, that everyday pressures tend to crowd out memory or knowledge of details of the basic scientific background to which the student must apply himself to provide a sound foundation for his technology, as we did in our day.

This is a good book. It starts by a sound "guide to students" on scientific and technical attitudes and practical things such as proper note recording and study disciplines, and proceeds to comments on safety, fire precautions and first aid in accidents. Then to the structure of matter, covering states of matter, kinetics, atoms and molecules, valency, symbols and formulae, atomic weights, equations, gas reactions, atomic structure, chemical bonds, ions, shapes of molecules, mixed crystals, pure and impure materials, etc, etc including a final note on zone refining—brief, informative and well illustrated by diagrams. Indeed so much is covered by this book that it is difficult to avoid the review becoming simply a catalogue for fear of omitting subjects which are mentioned, however briefly, and failing to give an adequate impression of the wide coverage.

"Energy" for example, is described via units for physical and chemical measurements and calibration of apparatus, work and energy, kinetic and potential, and the energy of physical and chemical changes, including heat changes during chemical reactions and measurement of energy changes, including calorimetry. The sound and simple treatment of "electricity and electrochemistry" is typical of the approach, not too little not too much, differentiating the behaviour of metals and non-metals and passing from electrical conduction to the effects of an electric current, to conduction by solutions, electrolysis, cells, etc and taking in the "redox" concept as well as analytical methods dependent on electrical phenomena.

By this stage the book, having dealt with the essential character of matter and some of its manifestation, is ready to press forward to rates of reaction and equilibria. Chapter five deals with equilibria, with later chapters on gases and liquids, periodic table, organic chemistry, analysis, methods of separation and purification, physical measurements, and introduction to statistics.

Maybe there could be a temptation to say that all this is in the text books, but not all of it is in one text book for one purpose, and a purpose clearly stated in the preface; moreover a purpose which is immediate to present training circumstances.

S. H. BELL

Student Review

The theory of functionality: Part I

By A. R. H. Tawn

Cray Valley Products, St. Mary Cray, Kent

First principles

The theory of functionality, which serves to unify so much of one's thinking about polymer formation, polymer properties and gelation, is variously attributed to R. H. Kienle and W. H. Carothers, some of whose contributions in the years 1928-1936 are discussed in this month's Editorial. Certainly, it was first given mathematical expression by Carothers, who denoted functionality by the symbol f and related it to degree of reaction p and degree of polymerisation x. Carothers developed his relationship between the quantities with particular reference to polycondensation and, for simplicity, it is proposed here to follow his example in the first instance, though the theory is a general one, applicable to both condensation and addition polymerisations.

The functionality of a system is qualitatively critical in determining the nature of the reaction product. It cannot be expressed out of context of the reaction which the system is to undergo, i.e. f can only be deduced if the nature of the reaction is known. Within this context, however, the functionality of a molecule is unambiguously defined as the number of other molecules to which it can be joined directly *via* the postulated reaction, *i.e.* the number of functional groups present on that molecule which can react under the chosen conditions. Thus, in a reaction, such as an esterification, involving the carboxyl group of an acid and the hydroxyl group of an alcohol, the following molecules would have the functionalities shown

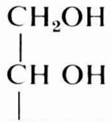
CH_3COOH
acetic acid
$f = 1$

$HOOC.C_6H_4.COOH$
phthalic acid
$f = 2$

$C_6H_3(COOH)_3$
trimellitic acid
$f = 3$

C_2H_5OH
ethanol
$f = 1$

HOC_2H_4OH
glycol
$f = 2$



$$\begin{array}{l} CH_2OH \\ | \\ CH\ OH \\ | \\ CH_2OH \end{array}$$

glycerol
$f = 3$

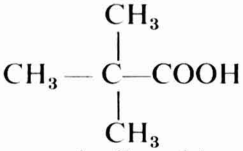
$CH_3(CH_2)_4\ CH = CH\ CH_2\ CH = CH(CH_2)_7COOH$
linoleic acid
$f = 1$

$CH_3CO\ COOH$
pyruvic acid
$f = 1$

$HOOC.CH = CH.\ COOH$
maleic acid
$f = 2$

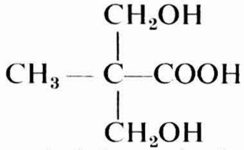
$HO(CH_2)_5\ COOH$
ε-hydroxy caproic acid
$f = 2$

Note that ε-hydroxy caproic acid is both an acid and an alcohol. Note also that the double bonds of linoleic and maleic acids, and the keto group of pyruvic acid, are not counted as functions in the context of an esterification reaction. They may well react in some circumstances according to some other mechanism, but they are not active in esterification. Consider also the compounds



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_3-C-COOH} \\ | \\ \mathrm{CH_3} \end{array}$$

pivalic acid



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{CH_3-C-COOH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

dimethylol propionic acid

At first view these appear to have functionalities in esterification of one and three respectively. But a carboxyl group attached to a tertiary carbon atom is slow to react under normal conditions of esterification. In the extreme, pivalic acid would not esterify and would then have to be assigned a functionality of 0 (like a hydrocarbon for example), whilst dimethylol propionic acid with its two reactive hydroxyl groups would behave as a diol ($f = 2$).

The examples of linoleic, pyruvic, maleic, pivalic and dimethylol propionic acids illustrate the importance of knowing the basic organic chemistry of a reaction system before trying to assign functionalities. Sometimes, as in the last two examples, there is a measure of uncertainty. Then, in order to get any answer at all, it becomes necessary to *assume* that a reaction will occur in a particular way. The most usual assumption made for purposes of simplification is that all functions of a given kind are equally reactive under the chosen conditions. Thus the secondary hydroxyl group of glycerol is known to be less reactive than the two primary hydroxyl groups. It does esterify, but at a slower rate. It is very difficult to allow for this when one tries to develop functionality theory quantitatively. Instead, one assumes that all three hydroxyl groups are equally reactive, and one maintains some mental reservations about the accuracy of any predictions made on this basis.

Behaviour of monofunctional reactants

The acetic acid molecule having one carboxyl group has a functionality of 1. The ethanol molecule having one hydroxyl group also has a functionality of 1. Esterification of acetic acid with ethanol may be termed a 1,1 reaction (though nowadays it is usual to replace this nomenclature by an expression of average functionality, *qv*). Complete reaction of all the acetic acid requires the presence of an equal number of moles of ethanol in accordance with the stoichiometry of the reaction. More fundamentally, one would say that the complementary functions OH and COOH must be present in equal numbers for complete reaction of both compounds to occur. If they are not, *i.e.* if one reactant is present in excess, that excess has nothing to react with, and will remain unreacted. This is elementary, and obvious in this instance; it is nevertheless emphasised, as it will later be seen that there are circumstances in which stoichiometric balance may be overlooked with disastrous consequences.

The important product of this particular esterification is ethyl acetate.

$$\mathrm{CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O.}$$

In this discussion it will be convenient to ignore the by-product of a condensation (water in this example). Being made up of two starting molecules or monomer units, ethyl acetate may, in the language of polymer science, be called a dimer. Nothing other than a dimer can result from a 1,1 reaction, for when it has been formed, no reactable functions remain, so no further reaction can occur.

Esterifications of phthalic acid with ethanol and of glycol with acetic acid are both reactions of monofunctional molecules with bifunctional molecules; they may be termed 1,2 reactions. Reaction stoichiometry requires that OH and COOH functions be present in equal numbers if an unreacted excess of one reactant is to be avoided. Hence 1 mole of glycol requires 2 moles of acetic acid, and 1 mole of phthalic acid requires 2 moles of ethanol. Both reactions proceed in two stages:

$$HOOC.C_6H_4.COOH + C_2H_5OH \longrightarrow \underset{\text{first product}}{HOOC.C_6H_4.COOC_2H_5}$$

$$HOOC.C_6H_4.COOC_2H_5 + C_2H_5OH \longrightarrow \underset{\text{second product}}{C_2H_5OOC.C_6H_4.COOC_2H_5}$$

$$HOC_2H_4OH + CH_3COOH \longrightarrow \underset{\text{first product}}{HOC_2H_4OOC.CH_3}$$

$$HOC_2H_4OOC.CH_3 + CH_3COOH \longrightarrow \underset{\text{second product}}{CH_3COOC_2H_4OOC.CH_3}$$

In each case, the first product results from the union of two starting molecules and may be called a dimer, whilst the second product results from the union of three starting molecules and may be called a trimer. At the trimer stage, all functional groups (OH and COOH) have been used up and the reaction cannot proceed further.

Similarly, it is easily seen that the ethanol-trimellitic acid reaction and the glycerol-acetic acid reaction are of the 1,3 type, and proceed in three stages to yield first dimer, secondly trimer and thirdly tetramer. At the tetramer stage, no functions remain so the reaction cannot proceed to build up bigger molecules.

The general conclusion is obvious: in any reaction between molecules, one of which is monofunctional and the other n-functional (a $1,n$ reaction), build-up of product molecules will cease when the n functions of the second molecule have each reacted with 1 function (and hence with 1 molecule) of the first. The ultimate product will thus be made up of $n + 1$ monomer units; it will be a $(n + 1)$-mer. Although it has been convenient to use the language of polymer science in discussing these reactions, none of them, of course, is regarded as polymerisation, since each leads to a clearly defined ultimate product of strictly limited molecular weight.

Bifunctional reactions

ε-Hydroxy caproic acid, possessing one OH group and one COOH group, is bifunctional in esterification. The OH group of one molecule can react with the

COOH group of a second molecule to form a dimer. Two bifunctional molecules are reacting together, so the reaction is of type 2,2.

$$\underset{\text{monomer}}{HO(CH_2)_5\,COOH} + \underset{\text{monomer}}{HO(CH_2)_5\,COOH} \longrightarrow \underset{\text{dimer}}{HO(CH_2)_5\,COO(CH_2)_5\,COOH}$$

The dimer also contains one OH group and one COOH group. It is also bifunctional, and again the OH group of one molecule can react with the COOH group of a second molecule to form a tetramer:

$$\underset{\text{dimer}}{HO(CH_2)_5\,COO(CH_2)_5\,COOH} + \underset{\text{dimer}}{HO(CH_2)_5\,COO(CH_2)_5\,COOH}$$

$$\longrightarrow \underset{\text{tetramer}}{HO(CH_2)_5\,COO(CH_2)_5\,COO(CH_2)_5\,COO(CH_2)_5\,COOH}$$

It is immediately obvious that the tetramer, like the dimer and monomer before it, is another hydroxy acid. Two molecules of tetramer can therefore combine by esterification to form an octamer and so on. Moreover, recalling the postulate that all functions of a given kind are conveniently regarded as being (or assumed to be) equally reactive, there is no reason why the OH group of, say, a tetramer, should not react with the COOH group of a monomer, or a dimer or . . . . Every species present in the reaction mixture always carries one OH and one COOH group, so every species is capable of reacting with any other. The results of this are twofold.

First, the reaction mixture will contain many different species because some molecules will not have reacted at all, some will have dimerised, some dimers will have reacted with other dimers to produce tetramers, some dimers will have reacted with monomers to form trimers, some trimers will have reacted with tetramers to form heptamers and so on. The further the reaction proceeds *i.e.* the greater the proportion of the original OH and COOH functions that have reacted, the greater will be the proportion of relatively large polymers in the reaction mixture. In other words, the greater the degree of reaction, the greater the average degree of polymerisation.

Secondly, however many reaction stages take place in this way, the product molecules always carry two functional groups and are therefore always capable of further reaction, and hence of further growth. This is a typical polycondensation reaction, and there is no obvious limit to the size of molecule which can be built up.

Finally, it will be observed that the reactive functions are always attached to terminal units; they never appear in the middle of the polymer molecule. This means that union of two molecules to make a bigger one can only occur end-to-end. Hence the polymer molecules must always have a linear chain-like structure.

A more commonly encountered type of bifunctional esterification is that which occurs between a dihydric alcohol and a dicarboxylic acid. This, and the quantitative application of functionality theory to bifunctional systems, will be dealt with in Part 2 of this series.

Irish Section

Student Group formed

On 23 September 1968 an informal meeting of Student Members of the Irish Section was held in Dublin.

At this meeting it was decided that a Student Group of the Irish Section should be formed. The meeting, which was attended by Mr R. Adam, Section Chairman, Mr G. F. Jones, Hon. Training Officer, Mr F. D. H. Sharp, Hon. Secretary and Mr A. Richards, together with Student and potential Student Members, was an opportunity for detailed discussion of the requirements of Student Members.

It was agreed that all student meetings should be held outside night school term time. Dates were fixed as follows:—

7 December 1968—subject—organic pigments
3 January 1969—subject—resins and varnishes
11 April 1969—subject—dispersion machinery

It was further agreed that the position be assessed after the third meeting with a view to arranging a full programme for the next session.

Organic pigments

Since then, on 7 December 1968, at the Clarence Hotel, Dublin, the Student Group has held its first technical session. Mr G. T. Williams, of the Pigments Division of Geigy (UK) Ltd., presented an excellent paper entitled "Organic pigments."

Mr Williams explained how the chemical groups of organic pigments affected the performance and properties of the materials. The talk was illustrated by a series of slides and panels.

As had been hoped by the committee this talk was designed to provoke discussion and in this aspect also the meeting was highly successful and the discussion produced many and varied questions.

On this occasion 14 students attended and Mr Adam, Section Chairman, presided.

F.D.H.S.

Resins for the paint and ink industries

The Second Meeting of the Student Group took place in the Clarence Hotel on 3 January.

Mr D. Godden presided and Mr M. J. O'Hanlon acted as Secretary. Fourteen student members attended the lecture.

Mr Godden welcomed the members and introduced the speaker, Mr H. C. Worsdall, of Surface Coating Synthetics Ltd., who began his lecture by saying that the problem of educating junior members was not peculiar to Ireland. He commented that he himself was on the Association's Working Party for Education, Training and Qualifications, which was discussing future steps in this field.

Mr Worsdall then outlined the various types of resins available to the paint and printing industries, such as natural, semi-synthetic and synthetic, and the various methods of manufacture of such resins.

In the discussion which followed this very informative lecture, Messrs. K. O'Callaghan, D. Barry, M. Granville, P. Fogarty and A. Richards took part and the lecturer was quite frank in his replies to the individual questions.

Mr Barry proposed a vote of thanks.

R.B.S.

Newcastle Section

Cathodic protection in conjunction with surface coatings

A meeting of the Student Group was held on 11 December 1968, when Mr F. R. Boynton, of International Paints Ltd., spoke on "Cathodic protection in conjunction with surface coatings."

Mr. Boynton outlined the principles of cathodic protection and then discussed the possible methods of application and the part each could play in preventing corrosion of the outer hulls of ships. For this purpose it was an economic necessity that cathodic protection should be used in conjunction with surface coatings.

Cathodic protection, and particularly overprotection, could have an adverse effect on many conventional shipbottom paints with the result that specialised coatings had to be developed. Laboratory and raft tests were described which had been designed to evaluate the performance of coatings under cathodic protection conditions. The general results obtained from these tests and in practice were also described. Saponifiable media gave poor performance even at normal potentials; coal tar and bituminous media were not saponifiable but tended to blister if overprotected. Chlorinated and other synthetic rubbers, epoxies, coal tar epoxies and zinc rich silicates performed well. In general, completely inert pigments and extenders should be used, though red lead was the preferred pigment for primers based on chlorinated rubber. Aluminium flake pigment was excellent for preventing water penetration of the film but it could fail by alkali attack if the paint was overprotected. This difficulty was largely overcome in practice by using anode shields of highly resistant coatings in the immediate vicinity of the anodes. In addition to making the cathodic protection effective over a much greater area of the hull the shields enabled bitumen aluminium paints to be used very successfully.

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.)

The Pigments Division of **Geigy (UK) Limited** has recently increased its customer service facilities by moving its technical service and application laboratories from Simonsway, Manchester, to larger premises at Wythenshawe, Manchester. The new laboratories were installed at Geigy's existing Wythenshawe site.

The new laboratories are divided into sections servicing the paint, plastics and printing ink industries, and are complemented by two physical laboratories. The emphasis is said to be on small scale equipment simulating that used in industry.

The Division's product and process development laboratories will remain at the manufacturing plant in Paisley, Scotland.

The Chemical Industries Association has recently published the 1968 edition of the directory "British chemicals and their manufacturers." New features include an improved section on group classification of companies' manufacturing activities. A grid format has been used, so that producers of a particular product range, or the product range of a particular company, can be easily determined.

Copies are available from the CIA free of charge to anyone genuinely interested in the purchase of chemicals and allied products.

It has recently been announced that the paint additives previously manufactured by **Byk-Gulden Lomberg GmbH** will now be manufactured by a new enterprise, **Byk-Mallinckrodt Chemische Produkte GmbH.** This results from the transferring of Byk-Gulden's Wesel works to **Mallinckrodt Chemische Produkte GmbH.**

An entirely new development in the field of high-build chlorinated rubber based coatings is claimed by **Inertol Company Limited,** a member of the Storry Smithson Group.

The new product, *Regnaclor*, is said to give outstanding performance for external or internal protection of concrete, cement render, asbestos cement and steelwork. It is claimed that single coatings 5mil or more thick are obtainable, and that *Regnaclor* is non-toxic, acid and alkali resistant and waterproof. A wide range of colours in both spraying and brushing consistencies is available.

It has recently been announced that **John Hall & Co. (1968) Ltd.** has been acquired by **Silexine Paints Ltd.** It is said that this will result in improved service and delivery schedules for Silexine in the South and South West.

Joseph Crosfield & Sons Limited has recently announced that a new plant for ester manufacture is now on stream. The new plant replaces a very much smaller one, and will greatly increase Crosfield's output of speciality esters.

A new booklet entitled "Amphionics and Ambiterics" has been published by **Glovers (Chemicals) Ltd.**

The booklet gives background information and details of Glovers' range of surface active agents. Copies are obtainable from Glovers on request.

ICI Ltd. has recently announced that its range of specialist paints, previously marketed under a variety of names, will now be sold under the name of *Dulux*. The changes of description will also indicate the nature of the product, e.g. *Permobel Chemical Resistant Finish* becomes *Dulux Epoxy Finish*, etc. No change in the composition of the products will be made.

Added to the *Dulux* range is a new white undercoat, claimed to have better "rubbing down" characteristics, and to allow smoother surface finish.

Also new from ICI is a new booklet on the use of *Alloprene* chlorinated rubber in paints.

A new principle in paint processing is claimed for the *Vibracon*, a new vibration mill produced by **Pilamec.** Cylinders, free to move axially, are centrifuged inside the chambers of a vibration mill moving in a circular path. A series of high-pressure annuli is created in which there is an intensive shearing action. The pigment particles are said to describe a helix as they move from one end of the annuli to the other. It is claimed that a pre-mix, when pumped through the annuli, emerges as a completely ground paint base.

The *Size 1 Vibracon* operates at rates around 250 litres per hour, and has two chambers, one above the other, which can be used in parallel for easy paint formulations, or in series for more difficult formulations.

A unit with about five times this capacity is expected to be marketed in 1969, and a laboratory version, the *Megacon*, handling 10-50 litres per hour, is available.

As from 1 January 1969, **Cray Valley Products Limited** has shown the decimal currency equivalents of the total value of invoices on all goods. This follows the setting up by Cray Valley Products of a study group to ensure the smooth transition to decimal currency throughout the company. As the time for change-over approaches, Cray Valley Products is to maintain a close liaison with its customers, to ensure that as little complication as possible is caused by the change-over.

A method of super-grinding titanium dioxide is claimed by **Pennsalt Limited.** The method uses a micronizer fluid energy grinding mill, using superheated steam through tangential holes in the circular grinding chamber, as the source of fluid energy.

Average particle sizes of 0.5 to 0.75μ are claimed.

Irish

Epoxy resins

The third meeting of this session was held in the Clarence Hotel, Dublin, on 29 November 1968. Twenty-nine members and seven visitors heard Mr W. V. Moore, of Shell Research Ltd., speak on epoxy resins.

Mr Moore began by describing the present uses of epoxy resins in the paint industry, together with the effects the method of manufacture of these resins had on the performance of the cured material. He also outlined the reactivity of the resins towards active hydrogen atoms and explained how use was made of this fact in forming densely cross-linked structures called curing agents.

A summary of the curing agents commonly used by the paint industry was given.

Various slides illustrating the formulation and properties of the amine-adduct and polyamide resin cured systems were shown. During the description of these slides, Mr Moore discussed the importance of surface preparation of the substrates prior to painting. In doing so, he stressed the importance of blast cleaning of steel which was to be used in severe conditions of immersion.

He also showed how the range of epoxy/amine cured systems was extended by mixing the resin with coal tar pitch. Formulations for such blends and their relative properties were discussed.

Mr Moore continued by describing epoxy ester resins, and their manufacture, and outlined the properties and advantages of paints based on these resins.

One interesting stoving system described was the so-called "three-component enamel" which consisted of an epoxy resin or epoxy ester, an alkyd resin and an MF resin. Such a system had better chemical resistance and mechanical properties than the normal alkyd/MF and did not suffer from lack of gloss retention as with epoxy stoving systems. Such a system was ideal for painting the exterior of drums, etc, where resistance to spillage, strong solvents and gloss retention were required.

Detailed descriptions of the epoxy/phenolic systems which had become the workhorse for the can-lining industry were given.

New developments included the use of complex amines for curing epoxy coatings, in temperatures as low as 0°C, and in high build systems. The difficulty which arose in the application of such coatings could be overcome by the use of heated two-component airless spray equipment.

In discussing powder coatings, Mr Moore illustrated formulations, and outlined methods of application such as the flock-gun, electrostatic spray, fluidised bed and electrostatic fluidised bed.

In concluding, he described the potentials of paints based on epoxy esters which were capable of being applied by the electrodeposition technique.

The quality of the lecture and the interest the audience had taken in it were clearly seen in the lively discussion which followed.

A selection of the questions raised is given.

Mr O'Callaghan asked the speaker for his opinion on the acid washing of concrete floors. Mr Moore said that application of 5 per cent solution of hydrochloric acid until effervescence had stopped, followed by thorough washing off of the acid and removal of loose material, was a good method. However, an easier and better method was to blast-clean the surface.

In answer to another question from Mr O'Callaghan, the speaker said that the application of a dilute solution of pva did not stop chalking of an epoxy system, and where freedom of chalk was desired it would be better to use an epoxy undercoat and a polyurethane finish.

Mr Patton asked the speaker for his view on the expected performance of a clear epoxy finish applied to exterior wood. It was felt that this would be bad.

Mr Darwin, inquiring about the minimum overcoating time of coal tar/epoxy with a conventional epoxy system, was told that an interval of a week was normal. He was also told that antimony oxide would not reduce the tendency of epoxy systems to chalk.

Mr O'Hanlon was informed that it was not recommended to apply epoxy paints to wet concrete.

Mr Stock asked what was the usual recoating procedure with an epoxy system which had chalked. Mr Moore suggested that chalking should be allowed to continue until the primer was exposed and then further coats of the epoxy finishing paint applied.

Mr Simon, in proposing the vote of thanks, said that he was pleased that Mr Moore had stressed the importance of surface preparation prior to the application of epoxy coatings.

R.B.S.

London

Aspects of the use of cellulose ethers in emulsion systems

A meeting was held at East Ham Technical College on Wednesday 15 January, with Mr J. Pooley in the chair, in the absence of Mr R. N. Wheeler. Dr Sven Lindenfors of Mo och Domsjö AB gave a lecture with the above title.

Dr Lindenfors said that there was some controversy over the important role of cellulose ethers in emulsion paints, so that formulation was still partly art and partly science. In particular there was much to be learned about adsorption on to the pigment and latex particles. The cellulose ethers were soluble in a wide range of solvents. It was generally accepted that the linear polymer molecules were partly coiled in solution, and the end-to-end dimension was made up of two factors, the size of the polymer unit, and the effect of the environment in extending or contracting the molecule. In a poor solvent, polymer/polymer interaction occurred; the chain would be shortened. An index of coil expansion was the molecular weight dependance of intrinsic viscosity, $(\eta) = KM^{\alpha}$. In a poor solvent, $\alpha = 0.5$, and in a good solvent, 0.8; if $\alpha = 2$ then one had a rigid rod-shaped molecule. Values of α ranged from 0.63 for methyl cellulose to 0.87 for hydroxy-ethyl cellulose in aqueous solutions. With sodium carboxymethyl cellulose, α depended on the ionic content of the solution, and could be 0.95 in 0.005 M NaCl.

Much theoretical information was obtained from dilute solutions, while latex paints contained much higher concentrations. By using a Monte Carlo technique, large scale models of polymer molecules had been made, and from these various parameters had been obtained, eg. the average diameter, the average length, and the average end-to-end distance. At higher concentrations there were various possibilities for the configuration of the polymer molecules, such as entanglement, parallel arrays, etc and such structures were responsible for elastic and viscous properties. There was a certain concentration necessary for the build up of a macromolecular network structure.

Adsorption experiments showed that a molecule of hydroxy ethyl cellulose could occupy an area of 80,000 Å^2 on a titanium dioxide surface, and the average coil length of the polymer was about 1,700 Å. It had been shown that ethyl hydroxy ethyl cellulose was less strongly adsorbed on titanium dioxide than sodium carboxymethyl cellulose. In practice, however, there was competitive adsorption on the pigment surface between the dispersant used and the cellulose thickener.

Dr Lindenfors dealt briefly with some of the technological factors affected by the choice of thickener, eg. can stability, penetration into porous substrates, levelling and sagging, and resistance to micro-biological attack. Following the discussion, a vote of thanks was proposed by Mr Merrington. a student at the college.

V.T.C.

Newcastle

Some analytical topics of interest to the paint industry

A joint meeting of the Newcastle Section with the North East Section of the Society of Analytical Chemistry was held at the Royal Turks Head Hotel on Thursday 5 December 1968. The Chairman for the evening, Mr Shenton, Chairman of the North East Section of the SAC, introduced four lecturers who spoke on some analytical techniques of interest to the paint industry.

The first speaker was Mr Goldsbrough of British Titan Products Co. Ltd. who gave a paper entitled "The use of scintillation counting for the investigation of adsorption phenomena in paints."

Mr Goldsbrough said that studies relating to the mechanisms involved in stabilising a dispersion of titanium dioxide pigment particles in air drying alkyd paints had been carried out by radiotracer techniques. Where appropriate, C14 labelled adsorbates including alkyd resins of differing mean molecular weight had been prepared in the laboratory.

Adsorption measurements were made after the suspensions had been shaken for periods of the order of a week to ensure complete equilibration. The pigment was removed from the paints by high speed centrifuging and the supernatant solution analysed by liquid scintillation counting. Care was exercised in order to avoid quenching and to check for the absence of chemiluminescence and self-adsorption.

Composite isotherms could be constructed for the various adsorbates, and information on the relative adsorption properties of these materials could be deduced.

The next speaker, Mr Deeley of ICI, spoke on the "Practical applications of the potassium bromide wedge and of interesterification techniques in paint analysis."

Mr Deeley stated that the potassium bromide wedge extended the use of differential infra-red spectroscopy from gases and liquids to solids. In infra-red analysis of paints, the organic binders, manipulatively speaking, were solids and their spectra could be very much simplified by using a wedge in the reference beam to remove the spectrum of a constituent of a mixture. Practical examples, including the quantitative use of the technique, were discussed.

He went on to discuss techniques involving interesterification with methyl acetate of the complex ester systems used as binders in paints, followed by gas liquid chromatographic recognition of the polyols and acids used. Finally practical examples of the use of the method on problems facing a paint analysis laboratory were discussed.

The third speaker was Mr R. A. Turner, of British Paints Ltd., who discussed "The detection and identification of residual solvents in thin paint films."

Surface coatings were known to retain solvents tenaciously, said Mr Turner, and it was therefore useful to know precisely the quantity of solvents retained in "dried" films.

A number of methods would be considered for the solution of this problem, and after suggesting various lines of approach, one simple method was described which had been used successfully to determine the amount and composition of solvent retained in coatings of polyurethane and epoxy systems.

In summary, a section of paint film on an aluminium substrate was vacuum distilled into a dry-ice trap from which the recovered solvent, homogenised with acetone, was analysed by gas-liquid chromatography, the total solvent content being taken as that which was volatile at 120°C at atmospheric pressure. This method should also be applicable to almost any other type of paint.

The final speaker was Mr Boynton of International Paints Ltd., whose subject was "The determination of the tributyl tin radical in sea water at the parts per million level."

Measurement of the rate of solution of poisons into sea water from anti-fouling paints was necessary to an understanding of their mode of functioning. This had proved particularly difficult in the case of organo-tin compounds as it entailed their determination at concentrations below the parts per million level.

Mr Boynton gave an account of several approaches to this problem, including amongst others gas-liquid chromatography, spectrophotometric methods after conversion to tin, and a biological method measuring toxicity. All the methods had severe limitations and as yet no method had been developed which appeared preferable to the biological method.

After question time the meeting was closed by Mr Shenton, who thanked the Newcastle Section for their hospitality.

A.L.

President's World Cruise—Full Report

11 November—10 December 1968

My wife and I were seen off at Southampton by Mr I. C. R. Bews and Mr R. H. Hamblin on 28 October 1968.

Owing to the threatened strike of engineering workers in Britain, certain maintenance work planned for the "Northern Star" had been postponed and a mechanical defect, which developed in one of the propellers after leaving Las Palmas, so much reduced the speed of the ship that it arrived several hours late at Cape Town. By the time it reached Fremantle the delay had increased to two days and instead of arriving on Sunday 24 November, it docked on Tuesday 26. Temporary repairs were carried out at Sydney and, to bring the ship back on schedule, the call at Auckland was cut out.

Because of these developments, it was necessary to modify at very short notice the programme which had been arranged with the various Sections of OCCA Australia and, in order to be on time for functions in New Zealand planned by the Wellington and Auckland Sections, we had to fly from Sydney to Wellington and then from Auckland back to Wellington to rejoin the ship.

Here, tribute must be paid to the valuable assistance of Mr K. M. Engelbert, Vice-President of the Association, in Durban, Mr Gavin Smith, President of OCCA Australia, and Messrs. James, Boroky, Kalwig and Scott, Chairmen of the West Australia, South Australia, Victoria and New South Wales Sections of OCCA Australia respectively, in reorganising at such short notice the arrangements made for meeting members of these various Sections and for the transfer of travel documents from one date to another at a time when bookings were extremely heavy owing to holiday traffic.

When we flew into Durban, we were met at the airport by Mr Engelbert, who was most helpful during the whole of our stay, showing us round the city and driving us to various points, including the palatial Edwards Hotel, where we were entertained at a smörgasbord by the Chairman, Mr P. A. Draper, and a number of Past Chairmen with members of the Committee and their ladies. The opportunity was taken during the evening to have a chat on Association and Section affairs with members of the Committee who were congratulated on the success of their recent Convention. They are seriously considering the organisation of an OCCA Exhibition and would welcome a visit from the Director and Secretary to discuss the running of such

OCCAA, West Australian Section Dinner Party (right to left) Mr F. Sowerbutts (President); Mrs A. James; Mr A. James (Chairman of the West Australian Section of OCCAA) with Messrs. Murphy and McKinnon and ladies

This and the other pictures are taken from Mr and Mrs Sowerbutts' own colour transparencies and the loss of quality in the transition to black and white is regretted.

a project, as well as other matters of particular interest to the Section. They would like this possibility to be considered by Council at an early date. On the following evening, before the ship sailed, some members went aboard to see the bound volume of illuminated addresses and congratulatory messages presented to the Association at the Jubilee Celebrations which had been taken with us for the benefit of the Overseas Sections. An OCCA wall plaque was presented to the Section with the good wishes of the Council.

At breakfast time on 26 November (two days behind schedule) we were met at the ship by Mr A. James, Chairman of the West Australian Section of OCCA Australia, who had driven to Fremantle that morning with his wife from their home at Bunbury, a distance of 120 miles. They devoted the whole of the day to showing us the beauties of Perth and the surrounding bush country and in the evening were joined by Messrs. D. McKinnon and P. Murphy, two members of the Section Committee with their ladies, who were the only members able to attend in view of the very short notice of the revised arrangements. Despite the small number present, a very jolly dinner party lasted until late that night, after which Mr and Mrs James drove the 120 miles back to Bunbury and then telephoned us early next morning to let us know that our revised flight arrangements had just been confirmed. The illuminated addresses were inspected with considerable interest.

The next day (Wednesday 27 November) we flew to Adelaide, where we were welcomed at the airport by Mr J. Boroky, Chairman of the South Australian Section of OCCAA, whose daughter presented my wife with a bouquet of magnolia. With them was Mr R. Paddick of Bell Publications, the Section's official photographer. A dinner was held that evening at the Hilton North Motel, North Adelaide, which was delightfully informal, and during that evening the 50th Anniversary scrolls were the subject of generous comment and admiration. After a friendly speech of welcome from Mr Boroky, cordial greetings and good wishes were extended on behalf of Council for the success of the Australian Association. In the course of informal discussions, here, as well as in West Australia, views were expressed by members on the move to independence of the Australian membership. The following day Mr Boroky drove us on a tour of the Borossa Valley, South Australia's wine growing area, with a visit to Gramps winery at Tarunda, as well as other places of interest in and around Adelaide, before our departure for Melbourne.

We were met at Melbourne on Friday 29 November by Mr Gavin Smith, who took us straight to our hotel and then drove us on a sight-seeing tour of the city. The Victorian Section's Annual Dinner had been held (as planned) two days earlier but despite this, Mr David Kalwig (Chairman of the Victorian Section) and his wife had assembled the Section Committee to meet us for cocktails and a very friendly luncheon at our hotel. In the afternoon, he and Mrs Kalwig accompanied us to the newly opened

Presentation of OCCA wall plaque to Mr G. Smith by the President. On the extreme right is Mr J. R. Rischbieth (Past Chairman of the Aust. Federal Comm.)

Art Gallery and Cultural Centre of Victoria, where the Director of the Gallery had made special arrangements for our visit and allocated an individual guide to point out the highlights of this highly sophisticated concept. It is easily the most magnificent gallery we have ever seen, either in this country or abroad.

In the evening, a buffet dinner had been arranged at the Clunies Ross Science Centre (opened earlier in the year by the Duke of Edinburgh) to enable us to meet officers of the Federal Council and their ladies. An OCCA wall plaque was presented to Mr Smith with cordial greetings from Council and here again the illuminated addresses from the Jubilee Celebrations were exhibited. The Victorian Section and the OCCA Australian Council have office facilities and filing cabinets in a room of this building which they share with other scientific societies, and it is here that they now hold their meetings. This extremely fine building with modern offices and lecture theatres is fully equipped for every conceivable type of projection and demonstration. Frank discussions took place with various members who were associated with the move for independence and the good wishes of Council were extended for the success of the independent Association.

On the following day, Mr Gavin Smith, with two of his children, drove us on the first 200 miles of our journey to Sydney, stopping en route at the Sir Colin MacKenzie Sanctuary, where about 140 species of birds, mammals and reptiles, all native to Australia, are to be seen in a setting of native bushland. He and his children left us at Albury, where we were to spend the night and returned to Melbourne.

The next day (Sunday) we continued our journey by inter-state coach to Canberra where we were met and shown the sights of the city by Miss Penfold, daughter of Mr A. R. Penfold, Honorary Member of both OCCA and OCCA Australia. Early on Monday 2 December we left by coach on the final stage of the journey to Sidney, where we were met and entertained to lunch by Mr and Mrs Penfold themselves.

The New South Wales Section of OCCAA had arranged a dinner for that evening at the Journalists' Club (where the Section now hold their meetings) for a party of about 40, including the ladies, and here we met Mr and Mrs John Scott (Chairman of the Section) and Mr and Mrs D. M. Stewart (President-Designate of OCCAA), together with several Past Chairmen and Committee members of the N.S.W. Section. As at the other Sections the commemorative scrolls were examined with interest and greatly admired. As a result of somewhat protracted arguments on relations past, present and future between OCCA and the independent body in Australia, it was suggested that there should be a more formal meeting with members of the

Meeting with members of the N.S.W. Section of OCCAA (left to right) Mr F. Sowerbutts (President); Mr Malcolm Stewart (President-designate of OCCAA); fourth from right, Mr John Scott (Chairman, N.S.W. Section, OCCAA)

Committee two days later and this was duly held, again at the Journalists' Club. A very frank discussion took place, centred largely on finance and the viability of the Association, as well as liaison with OCCA and kindred bodies. Stress was laid on the geographical disadvantages which exist in the case of the Overseas Sections and the Australians feel that the independent body is more suited to their requirements. They think that it will function satisfactorily and eventually flourish on the surplus accruing from their Conventions, social functions and the Raw Materials Index, but realise that their smaller Sections will require subsidising by the ones which are numerically stronger. The best wishes of Council were extended for their success. Mention must here be made of the help and kindness of Mr and Mrs Penfold and also of Mr E. T. Backous who conducted us to various points of interest in the city and devoted much of his valuable time to driving us to meetings. He, together with Mr Scott and Mr Stewart, saw us off at the airport when we left for Wellington.

At Wellington airport we were met by Mr and Mrs T. W. Slinn (Chairman of the Wellington Section) who took us to our hotel, where we were joined by Mr M. D. Thomson, a member of the Section Committee. The next day Mr Slinn showed us something of Wellington and drove us up the Hutt Valley, one of the nearby beauty spots. In the evening, there was a cocktail party at the home of Mr and Mrs Thomson for some 30 or more, including the ladies, at which we were able to meet members of the Committee and others. Here the Jubilee illuminated addresses and congratulatory messages were again displayed and a wall plaque presented to the Section on behalf of Council was received by Mr Slinn. The party then proceeded to Giovanni's Restaurant for a pleasantly informal dinner and dance.

On the following morning, in pouring rain, Mr and Mrs Slinn picked us up for a three-day drive to Auckland, where we were all due to attend the Section's Ladies Night on Monday 9 December. The programme was to travel that day as far as Wairakei via Wanganui and Chateau Tongariro, visiting various points of interest and the Geothermal Project en route but owing to "slips" and "washouts" (landslides and flooding) we found

Wellington Section Committee (right to left) Mrs T. W. Slinn; Mr T. W. Slinn (Chairman, Wellington Section); Mrs F. Sowerbutts; Mr F. Sowerbutts (President); Mrs M. D. Thomson; Mr M. D. Thomson (Hon. Social Secretary)

ourselves at the end of the day, after driving over 300 miles, at Palmerston North, some 93 miles from our starting point! Enquiries the next morning elicited the information that the east coast route to Wairakei via Napier, Rangitaiki and Taupo was possibly passable and this, fortunately, proved to be so. The Wairakei Hotel where we spent this second night is the venue of the New Zealand Sections' Conventions and is indeed a most suitable and pleasant location. The next day we continued on the final stage of the journey to Auckland, making a brief stop in Rotorua, and arrived in time for the Ladies' Night which was held in the magnificent South Pacific Hotel. There was a record attendance of about 120, including ladies and friends, and considerable interest was shown in the illuminated addresses which were prominently displayed during the evening. Mr G. J. Juster (Chairman of the Auckland Section) was presented with a wall plaque for the Section and greetings and good wishes were expressed on behalf of Council.

The President (Mr F. Sowerbutts) presents OCCA wall plaque to Mr G. J. Juster (Chairman of the Auckland Section) at the Ladies' Evening held in the South Pacific Hotel, Auckland

In view of our late arrival in Auckland, it was agreed that a meeting of the Section Committee—with Mr Slinn (Wellington) in attendance—should be held the next morning in a room which had been reserved at the airport, and various points of particular concern to the Section were discussed at length. These included the difficulties arising from geographical distance in relation to Wax Chandlers' Hall and certain aspects of finance. Most of the points raised were disposed of satisfactorily but it was agreed that a visit from the Director and Secretary of the Association, who would be more fully informed on details, would be mutually advantageous and this should be raised with Council.

After lunch at the airport we were seen off by Mr and Mrs Slinn, Mr and Mrs Juster and several members of the Auckland Section Committee. On arrival in Wellington we were met by Mr Gavin F. Browne (Publicity Officer of the Wellington Section) and later joined by Mr Thomson, both of whom accompanied us to the ship in time for its departure.

The kindness, co-operation and friendliness of the members in New Zealand was generous and special mention should be made of Mr and Mrs Slinn, Mr and Mrs M. D. Thomson, Mr Gavin Browne in Wellington and Mr and Mrs Juster in Auckland, together with Mr O. E. Rutledge (Treasurer) and Mr P. B. Hunt, a Past Vice-President of the Association.

F. Sowerbutts

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OCCA

TECHNICAL EXHIBITION

Since the list of exhibitors was published in the January issue of the *Journal*, there have been two further applications to exhibit which have been accepted by the Committee:

Stand 15A Redifon-Astrodata Limited.

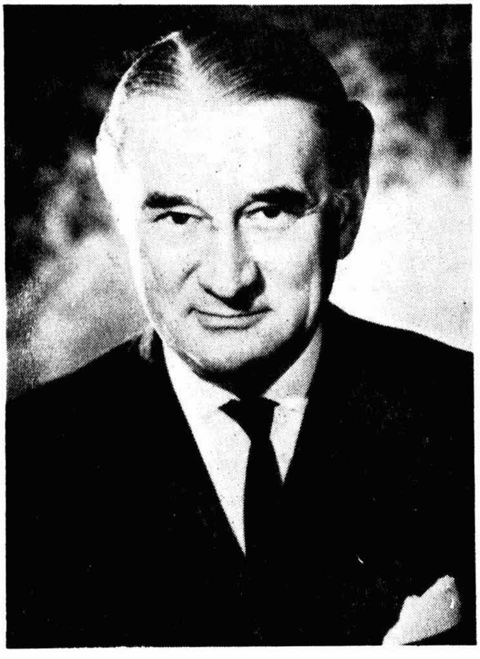
Stand 80 Dynamit Nobel Chemicals.

This means that this year's Exhibition will be the largest in terms of ground space since the Technical Exhibitions began in 1949. There will be 109 exhibitors, of which 12 have never previously participated in an OCCA Exhibition and 20 did not show at the 1968 Exhibition. Amongst the overseas countries from which exhibits will be shown are Belgium, Denmark, Finland, France, Germany, Holland, Italy, Norway, Switzerland and the United States of America. In all over 160 companies are mentioned in the *Official Guide*.

The venue is Alexandra Palace, and the times of opening will be as follows:

Monday 24 March	15.00 to 18.30hr
Tuesday 25 March	10.00 to 18.00hr
Wednesday 26 March	10.00 to 18.00hr
Thursday 27 March	10.00 to 18.00hr
Friday 28 March	10.00 to 16.00hr

A plan of the Hall can be found on page 275, and a numerical list of exhibitors on pages 271-72. A map showing the main routes to Alexandra Palace is on page 274; free car parking space is available, and a free bus service will run at frequent intervals between Wood Green station, on the Piccadilly Line, and the Exhibition.



Lord Kings Norton

The Exhibition Luncheon, for which the closing date for application for tickets is Monday 10 March, will be held at the Savoy Hotel at 12.45hr on Monday 24 March when Lord Kings Norton will reply to the Address of Welcome by the President. Lord Kings Norton will then open the Exhibition at 3 p.m. and afterwards make a tour of the stands.

The European Liaison Lecture, organised by the London Section, will take place at 18.00hr on Thursday 27 March at Alexandra Palace. The lecturer will be Dr Karl-Heinz Frangen, of Lackwerke Wulfing GmbH, who will speak on "Progress in electrodeposition in Europe." The closing date for application for tickets is Monday 10 March.

Copies of the *Official Guide*, which has already been sent to all members of the Association and exhibitors, will be available free of charge at the Information Centre, Stand 60, telephone 01-883 0120, or advance copies may be obtained from the Association's offices.

Invitations have again been extended to parties of senior science students from local schools to visit the Exhibition on the mornings of 25, 26 and 27 March. The visitors will be given a short introductory talk by a member of the Association before touring the stands. The Technical Education Stand, manned by representatives of technical colleges and from industry, will feature in the tour.

To assist the growing numbers of overseas visitors, and the exhibitors, interpreters will be available on Stand 59, or at the Information Centre.

In case of accident, British Red Cross personnel will be present on Stand 31.

Refreshment facilities at Alexandra Palace include several buffets and bars, which will be open throughout the period of the Exhibition, and two restaurants with full dining facilities: the Edinburgh Room, where tables can be reserved and which offers a wide choice of dishes, and the Alexandra Room, where tables cannot be reserved.

In conjunction with Grand Metropolitan Hotels Ltd., the Association has again arranged, as a service to visitors to the Exhibition, for accommodation at a 10 per cent reduction. All persons overseas receiving the *Official Guide* will find a form enclosed; others wishing to avail themselves of this service should write to the Association's Offices.

Latest Information

New Exhibitors

Stand 15a—Redifon-Astrodata Ltd., Brookside Avenue, Rustington, Sussex.

R.A.L. are exhibiting the recently launched production version of their automatic colour matching system, *Redi-Colour*. This is a special purpose computer for colour match prediction and shade correction for use in the paint, plastic and textile industries.

Special features of the computer are:—

> High speed operation by automatic data transfer and conversion, special Redifon "C" function for dark shade accuracy, easy to use controls, specially designed differential photometer and multiconcentration dye standardisation.

The equipment will be demonstrated throughout the exhibition and visitors are invited to bring their own trial samples for matching.

Stand 80—Dynamit Nobel Chemicals, 521 Troisdorf, Postfach 114-117, Germany.

Dynamit Nobel Chemicals, a manufacturer of world-wide status of dimethylterephthalate, will show their range of polyester resins for use in adhesives, lacquers and inks.

It is expected that special prominence will be given to *Dynapol*^{R} *L203*, a new saturated polyester which is claimed to have outstanding adhesive properties and good elasticity. It is said that lacquer films of *Dynapol*^{R} *L203* can be press-formed and deep-drawn, and are therefore particularly suitable for lacquering tinplate strip by roller coating. The films can be hot-sealed, are highly resistant to yellowing and are light resistant. By use of certain self-crosslinking resins sterilisable lacquer films can be produced having the same properties as a lacquer film of pure *Dynapol*^{R} *L203*.

Other applications are in printing inks, where good results are claimed in printing on plastic films, and for sintering powders for electrostatic and fluidised-bed coating techniques.

Technically qualified staff will be present on the stand to discuss applications of Dynamit Nobel products.

General

Stand 107—Beken Engineering Ltd.

It has recently been announced that E. Hunt & Co. Ltd., manufacturer of the *Beken* range of mixers, is to be known as Beken Engineering Ltd.

The details given in the *Official Guide* will otherwise be unchanged.

Stand 35—Silverson Machines Ltd.

A new addition to Silverson's range of high speed multipurpose mixer emulsifiers, the laboratory model, will be shown.

The new mixer incorporates a larger frame of conical tubular construction for maximum rigidity, and has 0.75in, 1in and micro attachments, for mixing in vials, universal bottles etc., which are interchangeable with the new frame. De Luxe models are also available.

The design of the knuckle (column clamp) on all models has been improved, and effortless positioning is claimed.

The machine is supplied complete with the standard range of processing heads, other specialised heads being available according to requirements.

A heavy-duty version of the de-luxe model is available.

Stand 57—International Colloids Ltd.

Included in the *Plastosperse* range of pigments dispersed in plasticisers for use in the manufacture of plastisols, vinyl films, pvc cable insulation etc. will be *Plastosperse 40*, a very high-jet carbon black. This product is said to offer considerable economies in use, as it contains 40 per cent w/w high-jet carbon, 10 per cent more than is usual in carbon dispersions for this application. In spite of the high carbon content, *Plastosperse 40* has a relatively fluid consistency.

Stand 60—Vinyl Products Ltd.

An entirely new range of styrene-acrylic emulsions, for use as paint-vehicles, will be introduced on the stand. Information will be available on pigment binding power, cost-efficiency, weathering properties and alkali-resistance compared with conventional paint emulsion, including all acrylics. Examples of the many important applications of the new media will be included in the exhibit.

A further new feature will be a vinyl acetate copolymer emulsion, developed by the company's research and technical service laboratories, which is said to give brushable semi-gloss and lustre paints with excellent application properties, including good flow and good open time, and fast recoatability at both high and normal humidities. A display will illustrate the excellent finish obtained, and demonstrate the effect of formulation variables on performance.

Stand 75—Controsion Ltd.

A new electrostatic spraying apparatus, *Controsion Model 3002*, will be shown. The new model incorporates reversible polarity for either negative or positive charge, and controllable voltage output from 30 to 150kV.

It is a small portable unit, operated from any 13 or 15 amp power point, and fitted with a complete powder delivery system, so that no air compressor is required. This system allows immediate change from one product or colour to another, while a continuous stirring process ensures against clogging, and gives even flow of coating material.

Model 3002 can be used for applying many plastic powders, notably nylon powder, which has previously caused difficulties with conventional electrostatic spray units, and can be used on cold substrates.

Stand 93—Berk Ltd.

Amongst the information available on Berk's *Oncor* range of corrosion resistant pigments will be development work on the use of *M50* and *S25* in water-based systems with particular reference to electrocoat and straight dip methods.

The display of *AFCO* filter cartridges and associated products will feature a new restrainer, which enables *Snap-Ring* filter bags to be used where pressure drops of up to 50psi are encountered.

Also to be shown are the use of *Phelam* antifouling and fungicidal additive and other organomercurials in Berk's *Solupacks*, and *Strodec Super V8*, a new phosphated co-ester, claimed to have high emulsifying, wetting and detergent properties, and remarkable dispersing characteristics for all types of insoluble materials.

Stand 99—Spelthorne Metals Ltd.

Visitors to the stand will be able to see copies of the new technical manual published by Spelthorne to coincide with the opening of their new factory and laboratories.

Stand 95—Porter-Lancastrian Ltd.

Additional features on the Porter-Lancastrian stand will include:

an open topped aluminium mixing pan, the open top being reinforced with a mild steel hollow section ring, the pan being supported on a rigid mild steel framework, and fitted with castors and a handle for easy moving.

a 200 gallon rectangular mild steel tank for bulk transport of paints and chemicals, fitted for handling by fork lift truck or overhead lifting gear, and

a 180 gallon vertical cylinder transportable tank of aluminium sheathed in mild steel, and incorporating a separate pressure container of sufficient capacity to discharge the tank. Alternatively discharge can be carried out using compressed air from an external source. Handling can be by fork lift truck or overhead lifting gear.

All these tanks incorporate the Porter-Lancastrian feature of disposable plastic linings, eliminating the need for cleaning.

Also to be shown is a pneumatically operated paint stirrer which can be fitted to the standard range of *Portatanks*, and moved from tank to tank as required.

Stand 48—Mastermix Engineering Co. Ltd.

The emphasis on the Mastermix stand will be the *HVS* range of dispersers, available in *High Speed* and *High Torque* models.

On display will be 7½ and 25hp *High Torque* models, fitted with *Trifoil* blades. These machines are essentially for use with heavy paste materials, such as printing inks, mastics, adhesives etc., while the *High Speed* models, with saw-tooth blades, are for more fluid materials, such as paints and liquid inks.

Stand 101/2—Buckman Laboratories Inc.

It has recently been announced that the agency agreement with A. Revai & Co. (Chemicals) Ltd., was terminated as from 31 January.

Cornelius Chemical Co. Ltd. (Stand 11) have been appointed as Buckman's exclusive distributor to the paint industry as from 1 February.

Stand 4—Winkworth Machinery Ltd.

A new addition to Winkworth's range of mixers will be exhibited for the first time. The machine, a heavy duty laboratory masticator mixer, has been developed for the heavier duties of masticating and mixing which cannot be undertaken by the normal Z blade mixer. The masticator is of 1.5 pint size, with a 2hp driving motor, and is available with an adjustable ram-type lid to contain the ingredients in the mixing chamber for quick and thorough processing.

Special features include stainless steel construction of all contact parts, jacketed trough with cored rotor-blades for steam heating or water cooling, and adjustable stud-type packing glands at each blade shaft.

Stand 72—Plastanol Limited

An additional feature on the Plastanol stand will be a water-soluble gloss resin for air-drying applications.

The product is said to be at a very interesting stage of development, and will be shown with the intention of instigating discussion and comment.

Stand telephone numbers

Since printing of the *Official Guide*, the following telephone numbers have been received from the GPO:

Stand 14a—Kollmorgen (UK) Ltd.—01-883 5281

Stand 17—Millroom Accessories and Chemicals Limited—01-883 5299

Stand 48—Mastermix Engineering Co. Ltd—01-883 5348

Stand 85—Jenag Equipment Limited—01-883 5344

Numerical List of Exhibitors—21 OCCA

Stand	
1	Armour Hess Chemicals Ltd.
2	Herbert Smith & Co. (Grinding) Ltd.
3	Diaf A/S
4	Winkworth Machinery Ltd.
5	Research Equipment (London) Ltd.
6	Eastman Chemical International AG
7	Hygrotherm Engineering Ltd.
8	Daniel Products Company
9	Vuorikemia Oy
10	Industrial Colours Ltd.
10	Sericol Group Ltd.
11	Cornelius Chemical Co. Ltd.
12	Lancashire Tar Distillers Ltd.
13	Microscal Ltd.
14	Harold Heydon & Co. Ltd.
14a	Kollmorgen (UK) Ltd.
15	Peter Silver & Sons (Engineers) Ltd.
15a	Redifon-Astrodata Ltd.
16	Sawell Publications Ltd. (*Paint Technology*)
17	Millroom Accessories & Chemicals Ltd.
18	VVB Lacke und Farben
19	Ciba (ARL) Ltd.
20	Ciba Clayton Ltd.
21	Degussa
22	Bush, Beach & Segner Bayley Ltd.
23	Laporte Industries Ltd.
24	William Boulton Ltd.
25	Morris Ashby Ltd.
26	Amalgamated Oxides (1939) Ltd.
27	Maschinenfabrik Heidenau, Veb.
Stand	
27	Unitechna GmbH
28	Marchant Bros. Ltd.
29	Marchant Bros. Ltd.
30	Carless, Capel & Leonard Ltd.
31	British Red Cross Society
32	W. A. Mitchell & Smith Ltd.
33	Unilever-Emery NV
34	SCC Colours Ltd.
35	Silverson Machines Ltd.
36	Rudolph Meyer's Inc.
37	Younghusband Stephens & Co. Ltd.
38	Geigy (UK) Ltd.
39	BASF United Kingdom Ltd.
40	Kingsley & Keith (Chemicals) Ltd.
41	Allied Chemical Corporation
42	Scado-Archer-Daniels NV
43	Norwegian Talc (UK) Ltd.
44	J. H. Little & Co. Ltd.
45	Technical Education
46	Union Carbide Europe SA
47	Novadel Ltd.
48	Mastermix Engineering Co. Ltd.
49	Amoco Chemicals Europe
50	D. H. Industries Ltd.
51	AMF International
52	Lennig Chemicals Ltd.
53	Scholven-Chemie AG
54	Chemische Werke Huels AG
55	*Paint Oil & Colour Journal*
56	Styrene Co-Polymers Ltd.
57	International Colloids Ltd.
58	National Provincial Bank Ltd.
59	Interpreters

Numerical List of Exhibitors—21 OCCA—*continued*

Stand	
60	Oil & Colour Chemists' Association Information Centre
61	Shell International Chemical Company
62	British Titan Products Co. Ltd.
63	Titanium Intermediates Ltd.
64	Paint Research Station
65	Surface Coating Synthetics Ltd.
66	Vinyl Products Ltd.
67	Anchor Chemical Co. Ltd.
68	Holmes Bros. Paint Machinery Ltd.
68	Torrance & Sons Ltd.
69	Imperial Chemical Industries Ltd.
70	Farbenfabriken Bayer AG
71	Rhone-Poulenc/Redis
72	Plastanol Ltd.
73	BP Chemicals (UK) Ltd.
74	NV Tiofine
75	Controsion Ltd.
76	Norsk Spraengstofindustri A/S
77	Victor Wolf Ltd.
78	Ferranti Ltd.
79	Molteni Off. Mecc. of Milan
80	Dynamit Nobel Chemicals
81	Morgan-Grampian (Publishers) Ltd. (*Paint Manufacture*)
82	British Celanese Ltd.
83	Farbwerke Hoechst AG
83	Hoechst-Cassella Dyestuffs Ltd.
83	Hoechst UK Ltd.
84	Sheen Instruments (Sales) Ltd.
85	Jenag Equipment Ltd.
86	Elcometer Instruments Ltd.
87	BIP Chemicals Ltd.
88	Kronos Titanium Pigments Ltd.
89	Phthalic Anhydride Chemicals Ltd.
89	United Coke & Chemicals Co. Ltd.
90	Hercules Powder Company Ltd.
91	Fredk. Boehm Ltd.
92	Premier Colloid Mills Ltd.
93	Berk Ltd.
94	Sachtleben AG
94	Pigment-Chemie GmbH
95	Porter-Lancastrian Ltd.
96	Victor Blagden & Co. Ltd.
96a	SPCM Matieres Colorantes de Mulhouse
97	Synthese NV
98	Columbian International (Great Britain) Ltd.
99	Spelthorne Metals Ltd.
100	H. Haeffner & Co. Ltd.
100	Swada (London) Ltd.
101	Buckman Laboratories Inc.
102	Buckman Laboratories Inc.
103	Joyce, Loebl & Co. Ltd.
104	Vibro-Mac s.a.s. di dr. E. Meazzi & Co.
105	RK Chemical Co. Ltd.
106	*prüfbau*
107	Beken Engineering Ltd. (formerly E. Hunt & Co. Ltd.)

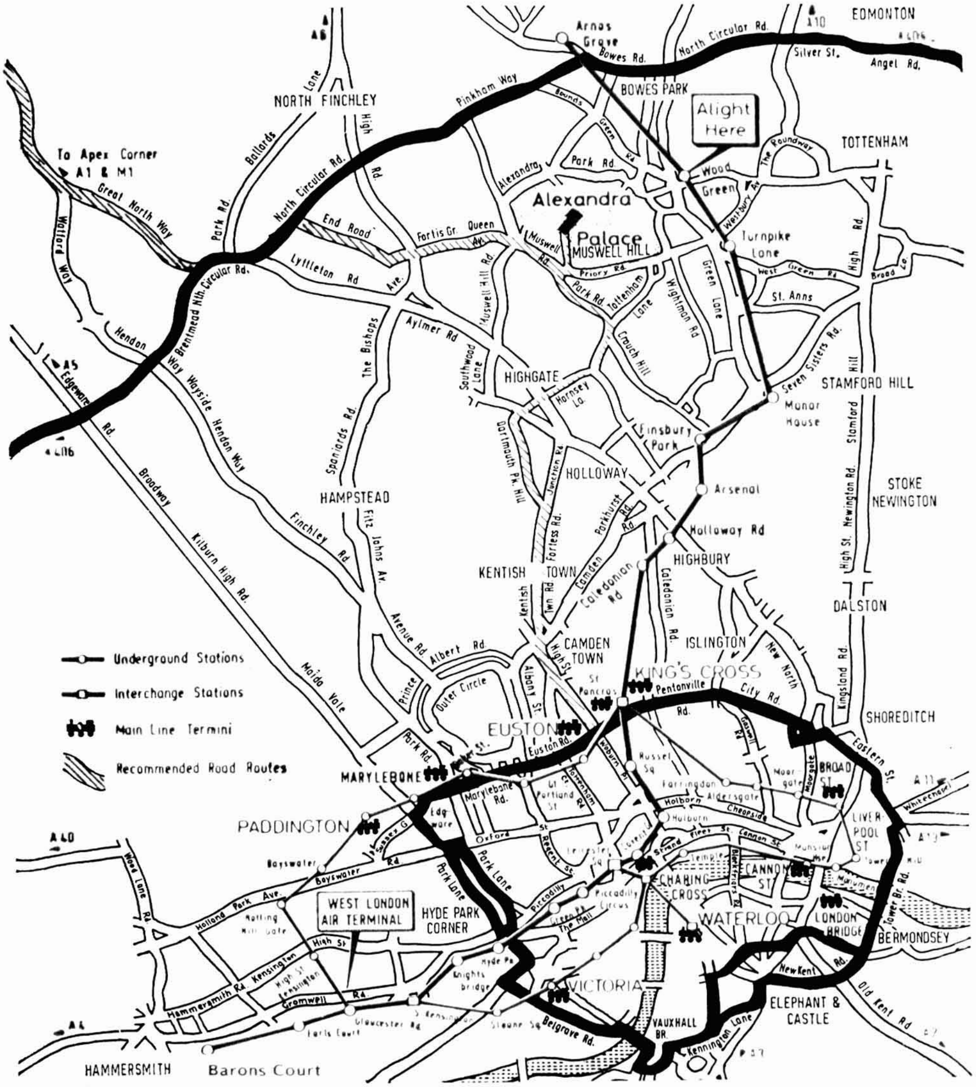
As well as exhibitors, mention of the following companies is made in the *Official Guide*.

Stand	*Company*	*Official Guide Page No.*
50	Ateliers Sussmeyer	82
76	Barter Trading Corporation Limited	119
97	BCL Coatings Limited . .	153
88	Canadian Titan Pigments Limited	104
26	Canadian Zincoli Pigment Limited	50
96	Cargill Incorporated . .	61
75	Cerac Laboratories	77
20	CIBA Ltd.	74
40	Commercial Solvents Corporation	103
8	Daniel, F. K., Laboratories Inc.	79

Stand No.	*Company*	*Official Guide Page No.*
14a	Davidson & Hemmendinger Inc.	104
88	Derives du Titane SA	104
50	De Vree, J., and Co.	82
40	Diamond Shamrock Corporation	103
74	Durham Raw Materials Ltd.	153
8	Dussek Brothers Limited	79
6	Eastman Kodak Co.	84
40	English China Clays Sales Company Limited	103
86	Erichsen GmbH	85
79, 104	Erlich, G. J., Limited	116, 159
25	Fabriques de Produits Chimiques de Thann et de Mulhouse	60
68	Fishburn Printing Ink Co. Ltd.	155
49, 71	Greeff, R. W., & Co. Ltd.	52, 134
54	Greenham, Herbert G. F.	72
41	Harmon Colours Ltd.	49
44	Henkel International GmbH	108
53	Industria (Chemical Services) Ltd.	141
50	Kupper, Peter, AMK	82
71	KW Chemicals Ltd.	134
76	Lonabarc Limited	119
40	Macbeth Corporation	104

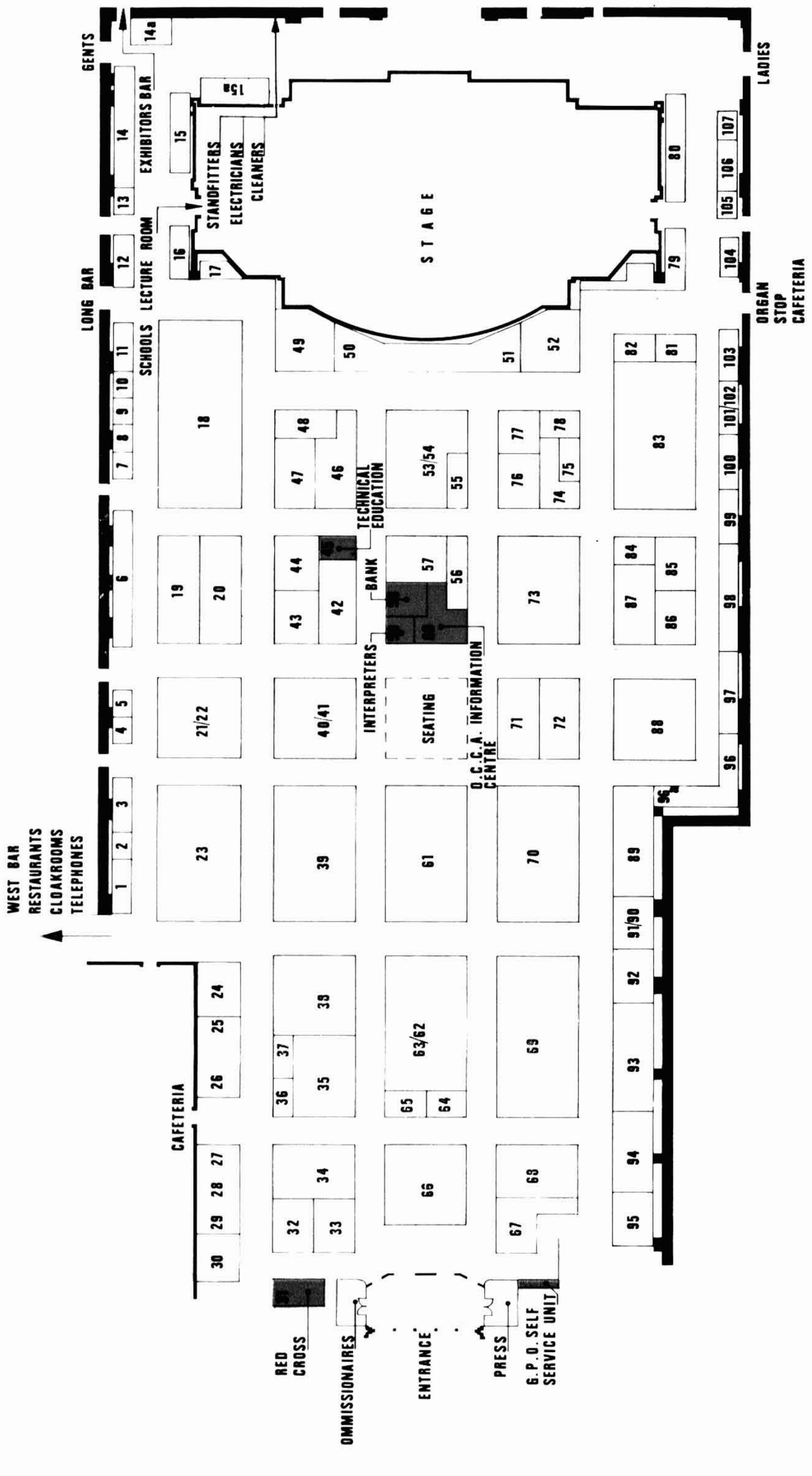
Stand No.	*Company*	*Official Guide Page No.*
67	Marbon Chemical Division of Borg-Warner Corporation	56
88	National Lead Company	104
96	Neville Cindu Chemie NV	62
47	Noury & Van der Lande NV	119
47	Oelwerke Noury & Van der Lande NV	119
50	Pamasol Willi Mader GmbH	83
71	Pechiney-Saint-Gobain	135
40	Pontyclun Chemical Company	102
65	Pope Chemical Corporation	150
83	Reichhold Albert Chemie AG	92
11	Roehm & Haas GmbH	78
98	Runnymede Dispersions Limited	76
40	The Sherwin-Williams Company	103
11	Sinclair Petrochemicals Incorporated	78
40	Staperm Limited	103
86	Stierand GmbH	85
26	Stolberger Zincoli GmbH	50
40	Swan, Thomas, and Company Limited	103
88	Titan Co. AS	104
88	Titangesellschaft mbH	104
40	Trojan Powder Company	103
22	Wacker-Chemie GmbH	69
40	Warwick Chemical (Yorkshire) Limited	103

HOW TO REACH ALEXANDRA PALACE



1. The free bus shuttle service will operate between Alexandra Palace and Wood Green Station on the Piccadilly Line (Underground), which is denoted by the thick red line.
2. Those travelling by road will find ample free car parking facilities at Alexandra Palace.
3. Visitors arriving at West London Air Terminal may board the Piccadilly Line trains at Gloucester Road Station.
4. The map also shows the position of the main line stations in relation to the Piccadilly Line.
5. It is hoped that the new Victoria Line will be opened in March, and this will give an additional link between Victoria and the Piccadilly Line.

Plan of Exhibition



Analysis of Exhibits

Exhibitor	Stand No.	Resins	Pigments	Extenders	Additives	Solvents	Oils	Machinery	Lab. Machinery	Instruments	Misc.
Allied Chemical Corporation	41	●	●								Low MW polyethylenes
Amalgamated Oxides 1939 Ltd.	26		●								
AMF International ..	51							●	●		
Amoco Chemicals Europe	49	●									Chemicals
Anchor Chemical Co. Ltd.	67	●	●	●	●						Curing agents for epoxide resins
Armour Hess Chemicals Ltd.	1				●						
Ashby, Morris, Ltd. ..	25		●	●							Natural bitumen
BASF United Kingdom Ltd.	39	●	●								Adhesives
Beken Engineering Ltd.	107							●			
Berk Ltd.	93		●	●	●						Filter cartridges
BIP Chemicals Ltd. ..	87	●									
Blagden, Victor, & Co. Ltd.	96	●	●	●							
Boehm, Fredk., Ltd. ..	91	●									
Boulton, William, Ltd. ..	24							●	●		
BP Chemicals (UK) Ltd.	73	●									Latices
British Celanese Ltd. ..	82	●			●						
British Titan Products Co. Ltd.	62		●								
Buckman Laboratories Inc.	101 102		●		●						
Bush, Beach & Segner Bayley Ltd.	22	●			●						Waxes

Exhibitor	Stand No.	Resins	Pigments	Extenders	Additives	Solvents	Oils	Machinery	Lab. Machinery	Instruments	Misc.
Carless, Capel & Leonard Ltd.	30	●				●					
Chemische Werke Huels AG	54	●				●	●				Terpolymer latex and pvc dispersions nylon coating powder
CIBA (ARL) Ltd. ..	19	●									
CIBA Clayton Ltd. ..	20		●								
Columbian International (GB) Ltd.	98		●								
Controsion Ltd.	75	●						●			dry lubricant, cermets, alloys
Cornelius Chemical Co. Ltd.	11	●	●		●						
Daniel Products Company	8				●			●			dispersions
Degussa	21		●	●							
D. H. Industries Ltd. ..	50							●	●	●	
Diaf A/S	3							●	●	●	
Dynamit-Nobel Chemicals	80	●									Adhesives
Eastman Chemical International AG	6				●						polyethylene dispersions
Elcometer Instruments Ltd.	86									●	
Farbenfabriken Bayer AG	70	●	●		●						
Ferranti Ltd.	78									●	
Geigy (UK) Ltd. ..	38		●		●						
Hercules Powder Co. Ltd.	90	●			●						
Heydon, Harold, & Co. Ltd.	14	●					●				

Exhibitor	Stand No.	Resins	Pigments	Extenders	Additives	Solvents	Oils	Machinery	Lab. Machinery	Instruments	Misc.
Hoechst UK Ltd. ..	83	●	●								
Hygrotherm Engineering Ltd.	7							●			
Imperial Chemical Industries Ltd.	69	●	●		●	●					
Industrial Colours Ltd. ..	10		●								
International Colloids Ltd.	57		●								Dispersions
Jenag Equipment Ltd. ..	85							●	●		
Joyce, Loebl & Co. Ltd.	103									●	
Kingsley & Keith (Chemicals) Ltd.	40	●	●	●							
Kollmorgen (UK) Ltd. ..	14a									●	
Kronos Titanium Pigments Ltd.	88		●								
Lancashire Tar Distillers Ltd.	12					●					Pitches
Laporte Industries Ltd. ..	23	●	●		●	●					Organic peroxides thixotropic agents
Lennig Chemicals Ltd. ..	52	●									
Little J. H., & Co. Ltd. ..	44	●			●	●					
Marchant Bros. Ltd. ..	28							●			
Maschinenfabrig Heidenau, Veb. ..	27							●			
Mastermix Engineering Co. Ltd.	48							●	●		
Meyer's Rudolph Inc. ..	36								●	●	
Microscal Ltd.	13									●	
Millroom Accessories & Chemical Ltd.	17							●	●		Mixing vessels

Exhibitor	Stand No.	Resins	Pigments	Extenders	Additives	Solvents	Oils	Machinery	Lab. Machinery	Instruments	Misc.
Mitchell, W. A., & Smith Ltd.	32	●									
Molteni Off. Mech. of Milan	79							●	●		
Morgan-Grampian (Publishers) Ltd.	81										Technical Journal
Norsk Spraengstofindustri A/S	76	●									bags for thixotropic alkyds
A/S Norwegian Talc (UK) Ltd.	43			●							
Novadel Ltd.	47				●						Resin intermediates
Paint, Oil & Colour Journal	55										Technical journal
Paint Research Station ..	64										Research Association
Plastanol Ltd.	72	●									
Porter-Lancastrian Ltd.	95										Storage tanks
Premier Colloid Mills Ltd.	92							●			
Prüfbau	106								●	●	
Redifon-Astrodata Ltd. ..	15a									●	
Research Equipment (London) Ltd. ..	5									●	
Rhone-Poulenc/Redis ..	71	●			●	●					
RK Chemical Co. Ltd. ..	105									●	
Sachtleben AG	94		●	●							
Sawell Publications Ltd.	16										Technical Journal
Scado-Archer-Daniels NV	42	●					●				
SCC Colours Ltd. ..	34		●								

Exhibitor	Stand No.	Resins	Pigments	Extenders	Additives	Solvents	Oils	Machinery	Lab. Machinery	Instruments	Misc.
Scholven-Chemie AG	53										Epoxy hardeners, raw materials for polyamides and polyurethane lacquers, waxes
Sheen Instrument (Sales) Ltd.	84									●	
Shell International Chemical Company	61	●				●					
Silver P., & Sons (Engineers) Ltd.	15							●	●	●	Benches
Silverson Machines Ltd.	35							●	●		
Smith, Herbert, & Co. (Grinding) Ltd.	2							●	●		
SPCM Matieres Colorantes de Mulhouse	96a		●								
Spelthorne Metals	99		●								
Styrene Co-Polymers Ltd.	56	●									
Surface Coating Synthetics Ltd.	65	●									
Swada (London) Ltd.	100		●								
Synthese NV	97	●									
NV Tiofine	74		●								
Titanium Intermediates Ltd.	63				●						
Torrance & Sons Ltd.	68							●	●		
Unilever-Emery NV	33				●	●					Plasticisers, lubricants, slip agents
Union Carbide Europe SA	46	●			●	●					
United Coke & Chemicals Co. Ltd.	89	●		●							Pitches and tars

Exhibitor	Stand No.	Resins	Pigments	Extenders	Additives	Solvents	Oils	Machinery	Lab. Machinery	Instruments	Misc.
Vibro-Mac s.a.s. di dr. E. Meazzi & Co.	104							●	●		
Vinyl Products Ltd. . .	66	●									
Vuorikemia Oy	9		●								
VVB Lacke und Farben . .	18	●	●	●	●						Plant
Winkworth Machinery Ltd.	4							●	●		
Wolf, Victor, Ltd. . .	77	●			●						
Younghusband Stephens & Co. Ltd.	37						●				

Eastbourne Conference

Film formation and curing

Members will have noticed that on the Lecture and Social Programme sent to them at the beginning of January it was stated that the registration forms must be returned not later than 1 April; the reason for selecting this date is that the allocation of hotel accommodation has to be made at that time.

Applications already have been heavy and members and visitors are therefore urged to send in their forms without delay.

Summaries of the papers and biographies of the lecturers were given in the January issue and additional copies of the summaries may be obtained, without charge, upon application to the Director and Secretary at the address shown on the front cover.

The usual social programme has been arranged and, as on previous occasions, the golf tournament will take place for the award of the "OCCA Conference Golf Trophy" presented by Mr S. Sharp, a member attached to the Hull Section.

The Conference will take place at the Grand Hotel, Eastbourne, from 17-21 June and the papers will be given in three morning sessions with additional workshop sessions on the afternoon of Wednesday 18 June. The Association's Annual General Meeting will take place on the afternoon of Friday 20 June.

West Riding Section

Annual Dinner and Dance—1968

The Tenth Annual Dinner and Dance of the West Riding Section was held at the Granby Hotel, Harrogate, on Friday 29 November 1968. The ever-increasing popularity of this function was clearly shown by the limiting of numbers to 230 and the willingness of guests to travel many miles to join in the festivities.

Mr L. H. Silver, the Section Chairman, in his Toast to the Ladies and Guests, remarked that this year's official guest

Seen at the West Riding Section Dinner Dance are (left to right): Mr D. Morris (Hon. Secretary, West Riding); Mr R. H. Hamblin (Director & Secretary); Mrs Morris; Mrs Smith; Mr T. R. Smith (Hon. Treasurer, West Riding); Mr D. T. Young (Social Secretary, West Riding); Mrs Chitty; Mrs James; Mr K. Chitty (Chairman, Thames Valley); Mrs Young; Mr D. M. James (Chairman, Newcastle); Mrs Newton; Mr W. F. McDonnell (Chairman, Manchester Section); Mrs McDonnell; Mr A. D. Ferns (President, Society Dyers and Colourists); Dr L. J. Watkinson (Vice-Chairman, West Riding); Mrs Silver; Mrs Miller; Mrs Watkinson; Mrs Ferns; Mr J. Miller (Chairman, Scottish); Mr L. H. Silver (Chairman, West Riding); Mr D. J. Morris (Chairman, Midlands); Mrs Morris; Mr D. S. Newton (Chairman, Bristol); Mrs Wheeler; Mrs Groom; Mr R. N. Wheeler (Chairman, London); Mr J. R. Groom (Committee Member, West Riding)

list was the largest in the history of the section. The Principal Guest, Mr A. D. Ferns, President of the Society of Dyers and Colourists, was joined by Mr R. H. Hamblin, Director & Secretary of the Association, and the Chairmen of the Bristol, London, Manchester, Midlands, Newcastle, Scottish and Thames Valley Sections, all accompanied by their ladies. The President of the

Association, Mr F. Sowerbutts, who was in Australia during his world cruise, sent a cable of congratulations. In concluding his short and very amusing toast Mr Silver made an intriguing offer to the ladies present—he guaranteed a very special gift to any lady who could produce her souvenir gifts from all ten dances provided each was accompanied by a paint-tin lid from a Yorkshire paint manufacturer.

Mr Ferns, in his response to the Toast, kept his promise to equal the shortness of the speech from the Chairman, and after thanking Mr Silver most charmingly for his kind comments, the proceedings were handed over to the toastmaster, Mr C. Butler, who quickly got the dancing under way.

Because of the large attendance, the band, who had been engaged to provide "music to dine to" as well as dance music, were unable to be accommodated in the dining room. As a result they offered to play past the originally scheduled deadline of 1 a.m., and as the evening was going with a real swing this offer was enthusiastically accepted. The festivities eventually ended at around 2 a.m. with coffee for those who had to drive home.

Tenth FATIPEC Congress

The tenth FATIPEC Congress is to be held in Montreux, Switzerland, from 7 to 13 June 1970.

FATIPEC was founded in Geneva on 8 January 1950, and it is particularly appropriate that the Swiss Association of Paint and Colour Chemists should be the hosts in its 20th Anniversary Year.

The theme of the Congress is to be "Resistance and deterioration of modern paint films, related to paint formulation, manufacturing process, application methods and surface treatment." For the printing ink industry, a complementary subject "The behaviour of printing inks in dependance of formulation, manufacturing, substrate and printing processes" has been chosen.

In chosing the theme, the stated objects of the organising committee are:

> " Past FATIPEC congresses have seen a majority of papers presented by the industries of raw materials, particularly those of binding agents and pigments. With this theme we hope to entice more chemists of the paint and printing ink industry to present papers based on their great experience in research, development and practical work.
>
> The 1968 FATIPEC Congress was mainly concerned with methods and equipment used in the paint and varnish industry.
>
> It will be interesting to see how these are used in practice, particularly with the latest methods of following the evolution of paint films after their application."

It is hoped that 60 lectures will be presented. Closing date for registration of a lecture is 30 June 1969, and for presentation of manuscripts 31 October 1969.

All correspondence concerning the lecture programme should be addressed to the President of the Scientific Committee:

Dr K. M. Oesterle,
Goldbacherstrasse 88,
CH 8700 Küsnacht/ZH,
Switzerland.

News of Members

Mr K. R. McDonald and Mr G. Myers, both Ordinary Members attached to the South African Section, have been appointed directors of BIP (SA) Pty, the resins manufacturing subsidiary of British Industrial Plastics Limited, with effect from 1 February.

Mr G. J. Wevell, an Ordinary Member attached to the South African Section, retired from the board as from 31 January, having served as a director since the company's formation in 1959.

Dr G. D. Parfitt, an Ordinary Member attached to the Midlands Section, has been appointed Hon. Secretary of the Colloid and Surface Chemistry Group of the Society of Chemical Industry.

Mr A. T. Radcliffe, an Ordinary Member attached to the London Section, and Technical Manager of Plastanol Limited, has recently been appointed a director of the company.

Register of Members

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

Ordinary Members

ARIES, ROBERT SANCIER, BSc, MS, MA, PhD, 69 rue de la Faisanderie, Paris 16, France. (*Overseas*)

ATKINSON, ERIC JAMES, 9 Bexhill Close, Pontefract, Yorks. (*West Riding*)

BATES, RONALD MARK, LRIC, 5 Lonnen Avenue, Fenham, Newcastle-upon-Tyne. (*Newcastle*)

BRADBURY, JEREMY ARD, 56 Windermere Road, Nr. Stockport, Cheshire. (*Manchester*)

BRENNAN, COLIN CHRISTOPHER GERARD, BA (Sc), ICI (Ireland) Ltd. (*Irish*)

BRIANT, ALAN MICHAEL, 14 Bankfields, Headcorn, Nr. Ashford, Kent. (*London*)

CRAKER, WILLIAM ERIC, BSc, PhD, 19 Hardy's Road, Cleethorpes, Lincs. (*Hull*)

EATOUGH, NEIL REDMAN, 11 Barnfield Avenue, Worsthorne, Burnley, Lancs. (*Manchester*)

HURREN, JOHN WILLIAM GEORGE, 24 Carlton Avenue, Billingham, Teeside. (*Newcastle*)

PARKER, JEFFREY MANSFIELD, 6 West Royd Villas, King Cross, Halifax, Yorks. (*West Riding*)

PENNE, ROGER ACHILLE, Hollestraat, Beerzel, Antwerpen, Belgium. (*Overseas*)

RIGBY, GEORGE EDMUND, BSc, 5 Victoria Road, Grappenhall, Nr. Warrington, Lancs. (*Manchester*)

SEN, RANENDRA KUMAR, BSc, 49, Lonsdale Road, Toronto 7, Ontario, Canada. (*Overseas*)

SIMMONS, JOHN ARTHUR, BSc, 27 Hughenden Road, High Wycombe, Bucks. (*Thames Valley*)

SOANE, GERALD DAMIEN, BSc, 22 Grassington Drive, Chipping Sodbury, Bristol BS17 6HW. (*Bristol*)

TOMKINSON, FREDERICK ROY, BSc, 27 Ravenstone Drive, Diggle, Nr. Oldham, Lancs. (*Manchester*)

WALKER, DAVID ANTHONY HALL, BSc, 246 Kings Road, Chorlton, Manchester. (*Manchester*)

Associate Members

ANDERSON, HEINE, BASF, (UK) Ltd., 84 Vaughan Way, Leicester. (*Midlands*)

BROWN, ROBERT JOHN, 56 Oxford Road, Salford 6, Lancs. (*Manchester*)

Student Members

BEWICK, GORDON, Camrex Limited, Tatham Street, Sunderland. (*Newcastle*)
CHARLES, DAVID, Camrex (Holdings) Ltd., 3 Tatham Street, Sunderland. (*Newcastle*)
COLLIN, IAN, Camrex Ltd., 3 Tatham Street, Sunderland, Co. Durham. (*Newcastle*)
DAVIS, PETER RICHARD, 151 Canterbury Avenue, Slough, Bucks. (*Thames Valley*)
KILDUFF, MICHAEL FRANCIS, Associated Printing Inks Ltd., Dunsinea Works, Ashtown, Co. Dublin. (*Irish*)
KITCHINGMAN, DENIS JAMES, T & R Williamson Ltd., Varnish & Enamel Works, Ripon, Yorks. (*West Riding*)
MIDWOOD, JOHN, T & R Williamson Ltd., Varnish & Enamel Works, Ripon, Yorks. (*West Riding*)
ROBERTSON, ANGUS, 2 Glassel Road, Lochwood E4. (*Scottish*)
SPENCER, ANTONY LEE, 12 Rossall Avenue, Chapelfield, Radcliffe, Lancs. (*Manchester*)
TODD, MICHAEL EDMUND, 127 Booth Street, Tottington, Nr. Bury, Lancs. (*Manchester*)
WATSON, GRAHAM CHRISTOPHER, 48 Oakland Street, Warrington, Lancs. (*Manchester*)
WILSON, ROBERT CAMERON, 41 Barrachnie Road, Garrowhill, Glasgow. (*Scottish*)

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.

Monday 3 March

Hull Section. "Present Developments in Driers" by a speaker from Hardman & Holden Ltd., to be held in the Bullock Lecture Theatre, Hull College of Technology, at 7 p.m.

Wednesday 5 March

London Section. Joint meeting with the Organic Finishing Group, Institute of Metal Finishing. "Insulation Coatings in the Electrical Industry," by R. Snadow of AEI, to be held at the Borough Polytechnic, Borough Road. London SE1, at 6.30 p.m.

Thursday 6 March

Newcastle Section. "Emulsion Paints: Instrumental Aids to Binder Selection," by Dr C. Bondy of Revertex Ltd., to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Monday 10 March

London Section—Southern Branch. "Paints, Preservatives and Water Repellents' Treatment for Timber," by Mr P. Whiteley of the Building Research Station, to be held at the Keppel's Head Hotel, The Hard, Portsmouth, at 7.30 p.m.

Tuesday 11 March

West Riding Section. "Ethylene-grafted Emulsions," by Mr K. A. Safe of Vinyl Products Ltd., to be held at the Griffin Hotel, Boar Lane, Leeds 1, at 7.30 p.m.

Thursday 13 March

Scottish Section. "Acrylic Resins," by Mr R. H. E. Munn and Mr A. R. H. Tawn of Cray Valley Products Ltd., to be held in the Whitehall Restaurant, Renfield Street, Glasgow, at 6.00 p.m.

Friday 14 March

Manchester Section. "Broad Trends in the Development of Building Assembly Systems," by Professor D. Harper of the Institute of Science & Technology, University of Manchester, to be held at the Liverpool Building & Design Centre Ltd. at 6.30 p.m.

Saturday 15 March

Scottish Section—Student Group. "Modern Managerial Techniques," by Dr D. Cameron of the University of Strathclyde, to be held at the Lorne Hotel, Sauchiehall Street, Glasgow, at 10.00 a.m.

Wednesday 19 March

Scottish Section—Eastern Branch. "Annual General Meeting," followed by a selection of films from the library of Shell Chemicals Ltd. To be held in The Wee Windaes Restaurant, 142 High Street, Edinburgh, at 7.30 p.m.

Thursday 20 March

London Section. "New Resin Systems for use in Coil Coating Applications," by L.A. Tysall of Shell Research Ltd., to be held at the New Engineering Block, University College, London WC1, at 6.30 p.m.

Midland Section—Trent Valley Branch. Joint meeting with Derby and Nottingham Branches of the National Federation of Master Painters and Decorators. "Timber and its problems as applied to Painting," by Mr G. S. Hall of the Timber Research Development Association. To be held at British Rail School of Transport, London Road, Derby, at 7.00 p.m.

Thames Valley Section. "Pigments—Particular Reference to Printing Inks," by Dr F. M. Smith of Geigy, to be held at the Royal White Hart Hotel, Beaconsfield, Bucks, at 7.00 p.m.

Friday 21 March

Midlands Section. Newton Friend Lecture. "Design and Fashion Through Chemistry." "Contribution of Science to Design and Fashion," by Mr M. W. Alford of Courtaulds Ltd., "Palettes of Fashion"—Film. To be held at the Chamber of Commerce House, 75 Harborne Road, Birmingham 15, at 6.30 p.m.

Thursday 27 March

London Section. "Progress in electrodeposition in Europe," European Liaison Lecture by Dr K. H. Frangen, to be held in the Alexandra Room, Alexandra Palace, London, at 6.00 p.m.

Friday 28 March

Bristol Section. "Operational Research," by W. C. Henshaw of the Bristol College of Commerce, to be held at the Royal Hotel, Bristol, at 7.15 p'm.

Irish Section. "An examination of Aqueous Interior Semi-Gloss Paints and the Development of an Aqueous Semi-Gloss Vehicle," by Mr J. H. Sparrow of Charles Lening & Co. Ltd., preceded by the Annual General Meeting at 7.30 p.m., at the Clarence Hotel, Wellington Quay, Dublin.

Wednesday 2 April

Manchester Section—Student Group. "New Polymers for Emulsion Paints," by Mr A. C. Fletcher of Vinyl Products Ltd., to be held at the Manchester Literary & Philosophical Society at 4.30 p.m.

Thursday 3 April

Newcastle Section. Annual General Meeting. To be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Monday 14 April

London Section—Southern Branch. Annual General meeting. To be held at the Keppel's Head Hotel, The Hard, Portsmouth, at 7.30 p.m.

Thursday 17 April

Midland Section—Trent Valley Branch. Annual General Meeting. To be held at Midland Design and Building Centre, Mansfield Road, Nottingham, at 7.00 p.m. Followed by "Colour

& Design," by Mr D. J. Healey of ICI Ltd., Fibres Division. Film: "Colour Sense."

Friday 18 April

Manchester Section. Annual General Meeting. To be held in the Pavilion Suite, Lancashire County Cricket Club, Old Trafford, Manchester 16, at 6.30 p.m.

Irish Section. "Metrication and What it Means," to be held at the Clarence Hotel Wellington Quay, Dublin, at 8.00 p.m.

Tuesday 22 April

West Riding Section. Annual General Meeting. To be held at the Griffin Hotel, Boar Lane, Leeds, at 7.30 p.m.

Wednesday 23 April

Scottish Section—Eastern Branch. "The use and development of pva Emulsions in the field of Paper Coatings, Paint and Adhesives," by Mr R. A. C. Kuenzli of Resinous Chemicals Ltd., to be held at The Wee Windaes Restaurant, 142 High Street, Edinburgh, at 7.30 p.m.

Thuesday 24 April

London Section. Annual General Meeting. To be held at the Criterion-in-Piccadilly, London W1, at 6.30 p.m.

Friday 25 April

Bristol Section. Annual General Meeting. To be held at the Royal Hotel, Bristol, at 7.15 p.m.

Midlands Section. Annual General Meeting. To be held at the Winston Restaurant, Balsall Heath Road, at 7.00 p.m.

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

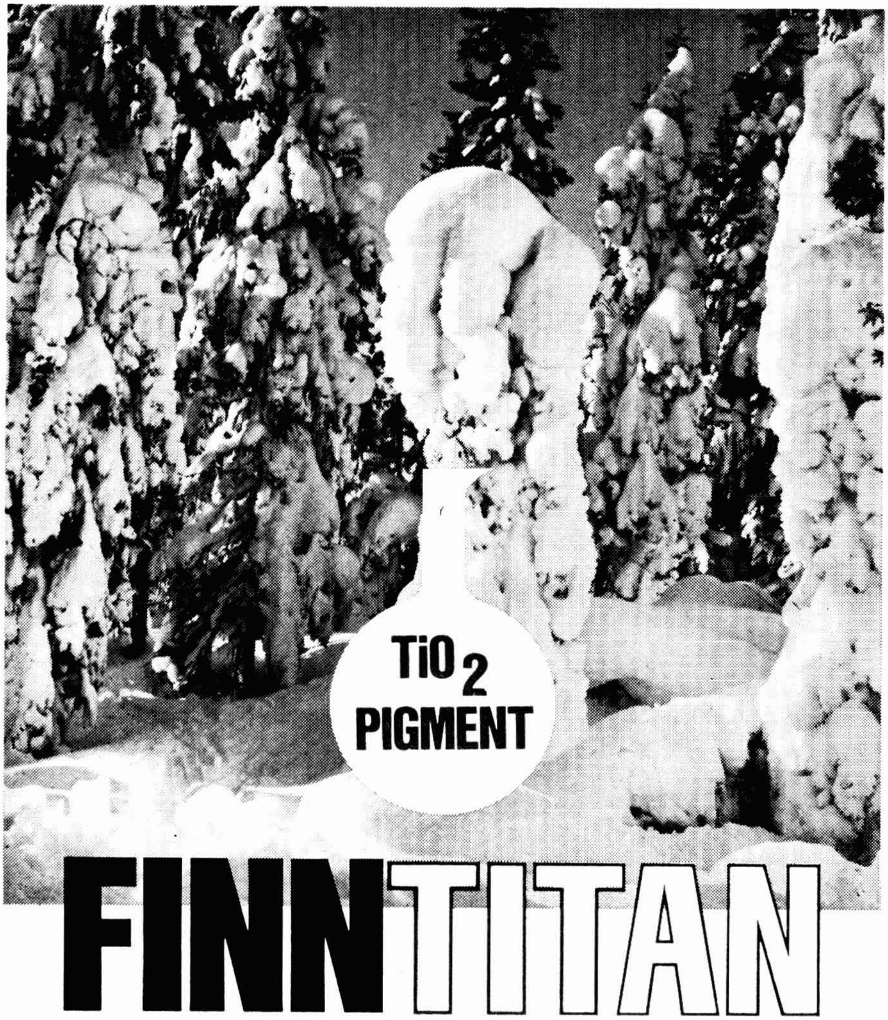
Journal of the Oil and Colour Chemists' Association. Published monthly. Subscription rate to non-members in UK and abroad, £7 10s. p.a. post free ; payable in advance.

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.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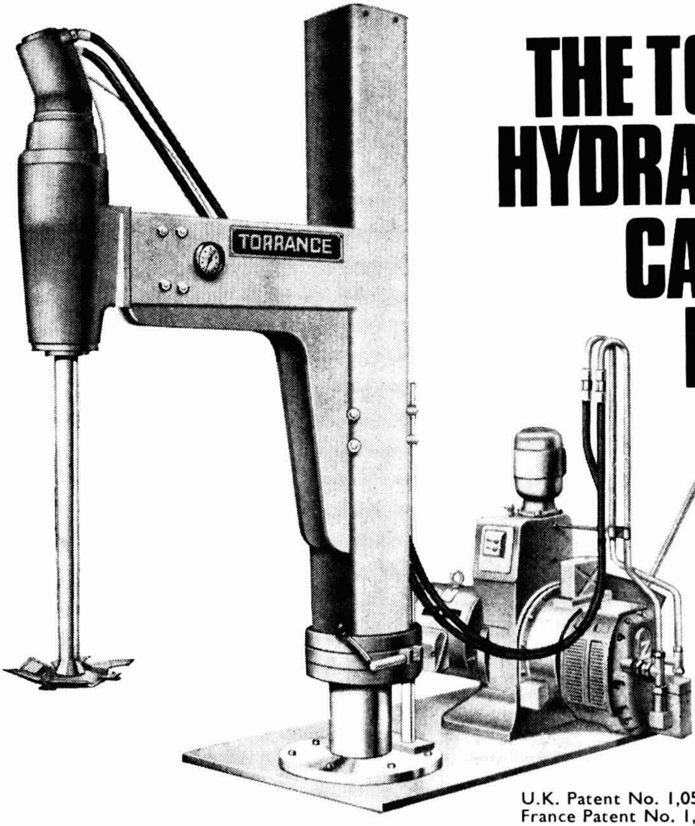

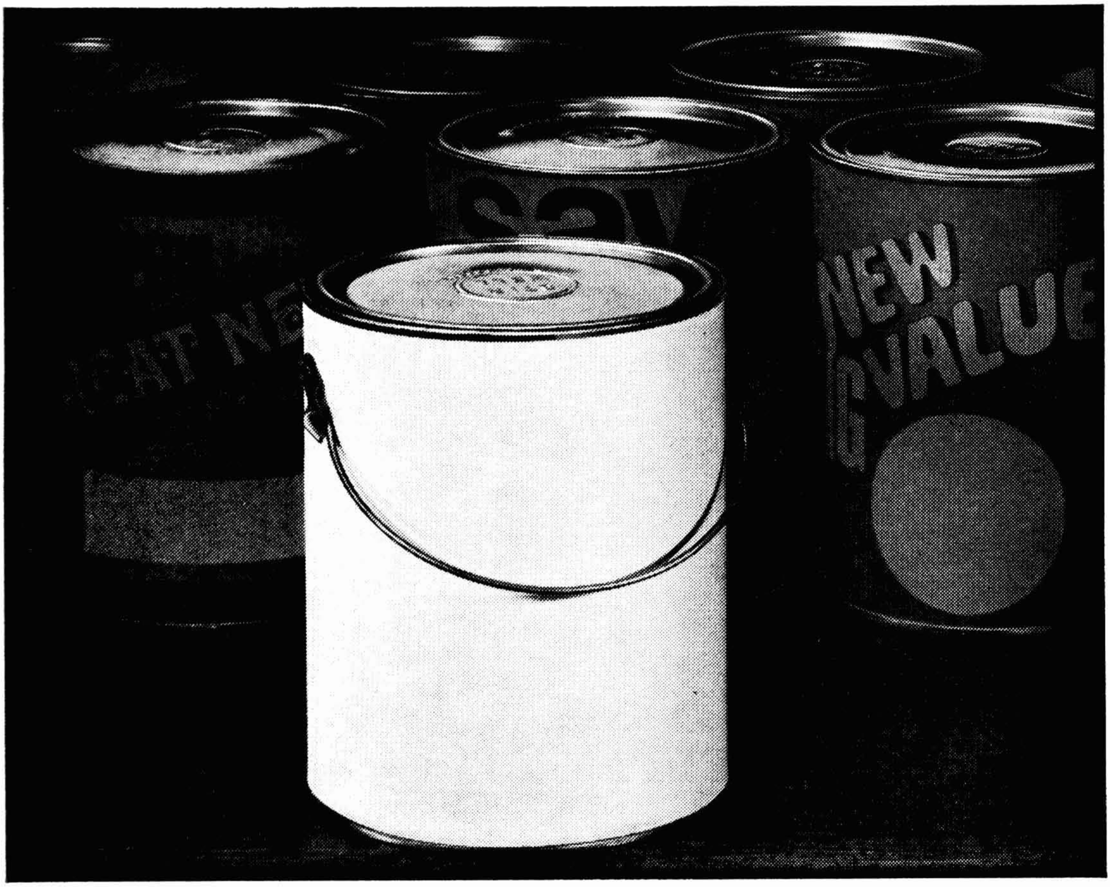
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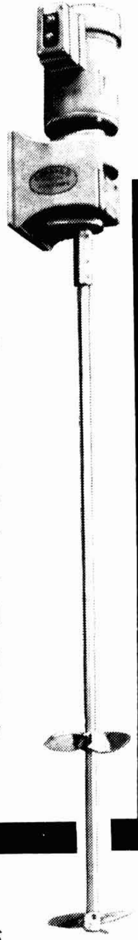

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about effective, efficient Nopco paint defoamers

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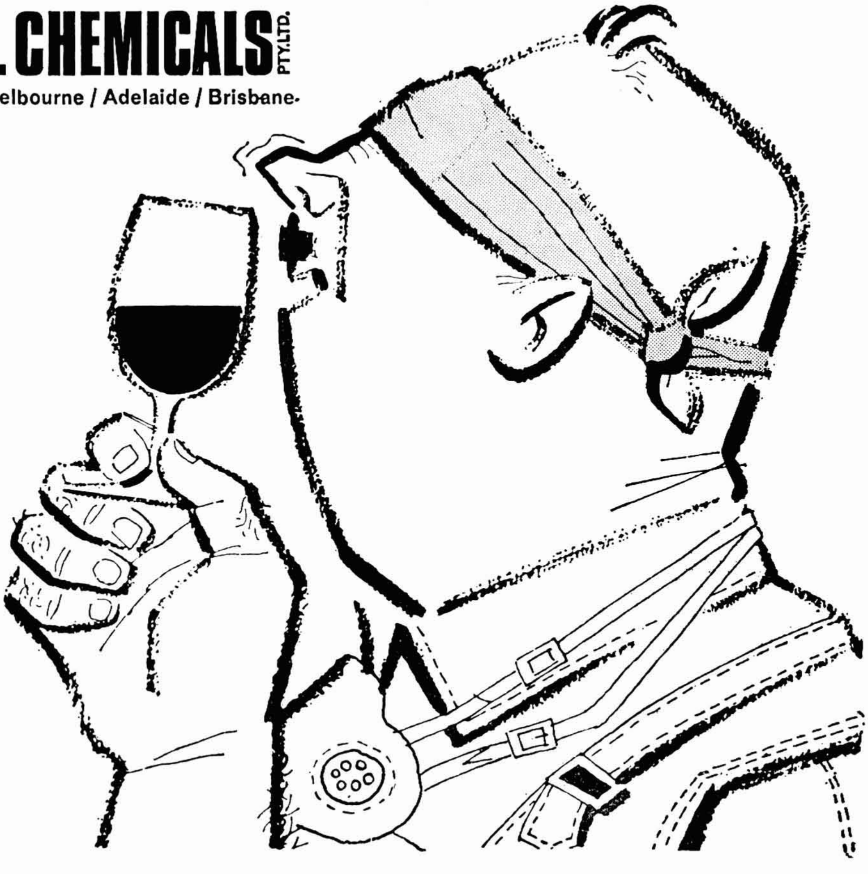

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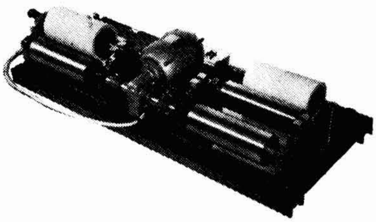

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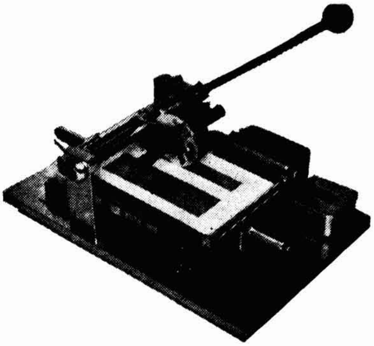

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introduction to paint technology

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.

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

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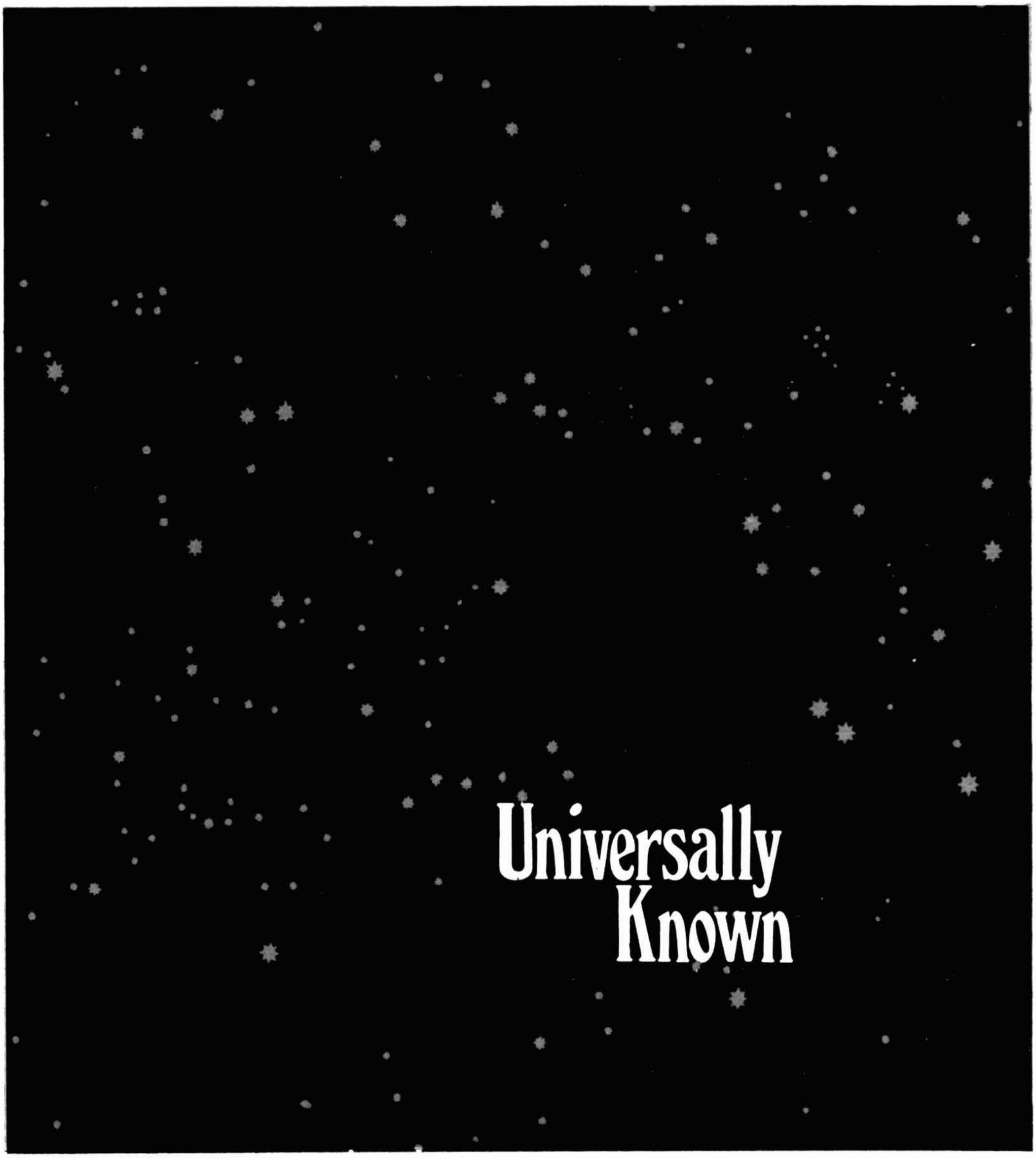
Including colour measurement, viscometers, brushability, hardness, film thickness, weatherometers, and use of computers.

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).

Printed in England by Metchim & Son Ltd., 8 Storey's Gate, Westminster, London, S.W.1.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