

# JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION



✓Vol. 47 No. 10

October 1964

*TRANSACTIONS AND COMMUNICATIONS*

WATER THINNABLE ALKYD MEDIA .. .. .	767
R. A. Brett	
THE EFFECTS OF MINERAL EXTENDERS ON ANTI-CORROSIVE PRIMERS BASED ON ZINC CHROMATE ..	799
P. Delfosse	
A METHOD FOR THE MEASUREMENT OF THE ADHESION OF SURFACE COATINGS UNDER SERVICE CONDITIONS ..	812
P. A. Walker	
QUEENSLAND HEALTH LAW IN RELATION TO PAINT AND RELATED PRODUCTS .. .. .	824
M. H. Gabriel	
<i>CORRESPONDENCE</i> .. .. .	831
<i>REVIEWS</i> .. .. .	836
<i>SECTION PROCEEDINGS</i> .. .. .	839
<i>INFORMATION RECEIVED</i> .. .. .	840
<i>NOTES AND NEWS</i> .. .. .	841

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

**5 - 4 - 3 - 2 - 1 - ZERO**

---

**FROM START TO FINISH USE**

***HEYDOLACS***

***THE***

***RESINS THAT COUNT***

---

---

**MADE BY HAROLD HEYDON OF COURSE**

*Write or telephone*

**AGENTS**

**UNIVERSAL SYNTHETIC**

**86 BOW ROAD, LONDON E.3**

**CO. LTD.**

**TELEPHONE :**

**ADVANCE 4781**



The  
**ESCOREZ**  
big new  
**ESCOREZ**  
name in  
**ESCOREZ**  
resins

**What does it mean to the paint industry?**

A great deal. Escorez resins: dissolve completely in non-aromatic hydrocarbons; are chemically inert; are light-stable, exhibit minimal yellowing; have good compatibility with a wide range of film formers; partly replace alkyd resins in decorative paints. Batch-to-batch consistency, first-class technical service and prompt delivery make Escorez resins, at only £100 per ton delivered, well worth investigating. If you would like more detailed information, please fill in the coupon below.

Please send me information about the use of Escorez resins in the paint industry.

NAME ..... POSITION .....

COMPANY .....

ADDRESS .....

*(Please use block letters)*



3

Return to: Esso Petroleum Co, Ltd • Chemicals Department • Victoria Street • London SW1

# Refined Soyabean & Linseed Oils

## Soya and Linseed Stand Oils

Boiled and Blown Oils

MASTIC OILS

“PLASTYBCOL”

&

# “CONJUGOL”

brand of Dehydrated Castor Oil for

“ALLOPRENE”\*/DCO Paints



## Younghusband Stephens & Co. Ltd

Sales Office : London Road, Barking, Essex

Telephone : Rippleway 3467-9

Cables : Paintoil, London

Telegrams : Litho, Barking

\*“ALLOPRENE”—chlorinated rubber I.C.I. Ltd., Mond Division

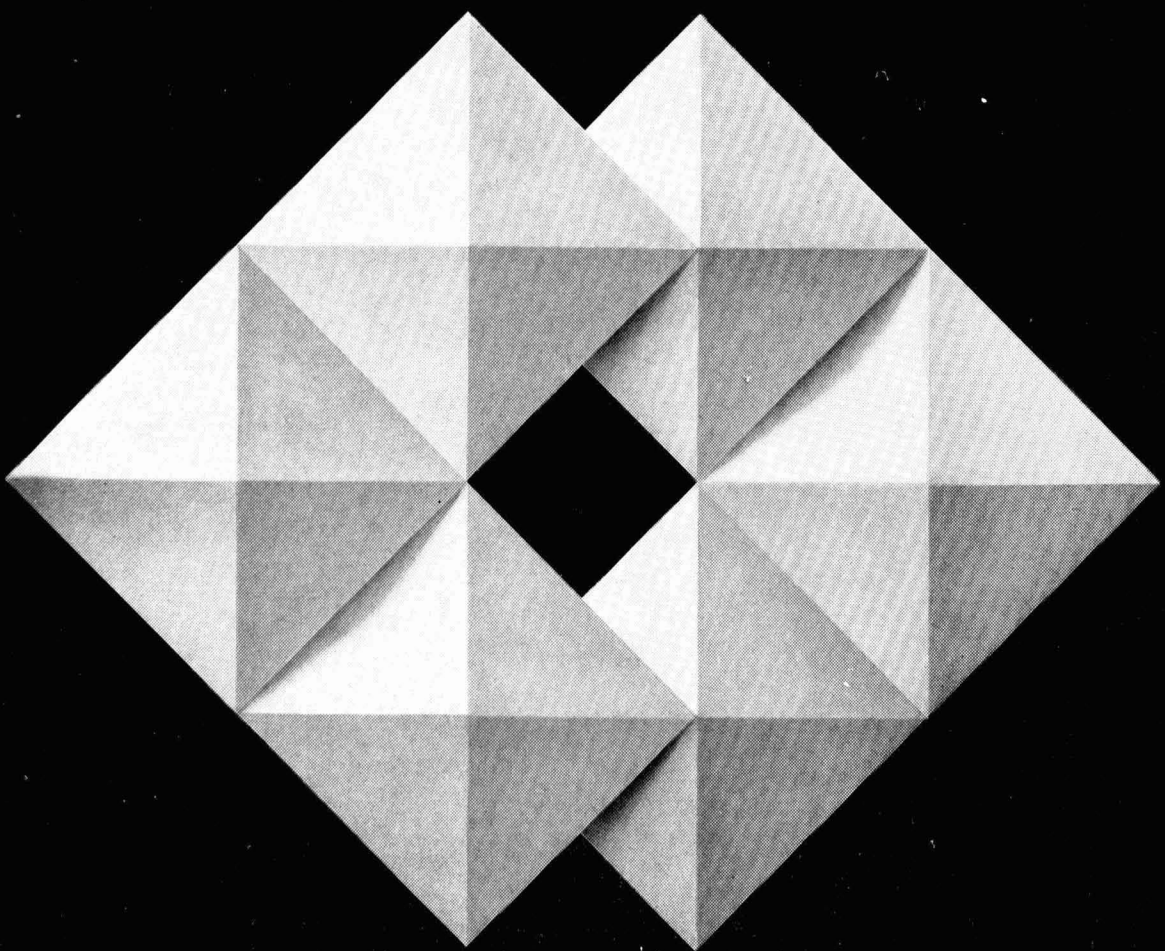
# KRONOS



# TITANIUM

CONSTANT QUALITY  
QUALITY CONSTANT  
CONSTANT QUALITY  
QUALITY CONSTANT  
CONSTANT QUALITY  
QUALITY CONSTANT

# DIOXIDE



KRONOS TITANIUM PIGMENTS LTD. · YORK HOUSE · 199 WESTMINSTER BRIDGE ROAD · LONDON S.E.1

DERIVES DU TITANE S.A.  
LANGERBRUGGE, BELGIUM

TITANGESELLSCHAFT MBH  
LEVERKUSEN, GERMANY

TITAN CO A.S.  
FREDRIKSTAD, NORWAY



# NUODEX DRIERS

*for all occasions...*



- ★ certified metal content
- ★ good colour
- ★ high purity
- ★ low viscosity
- ★ excellent stability

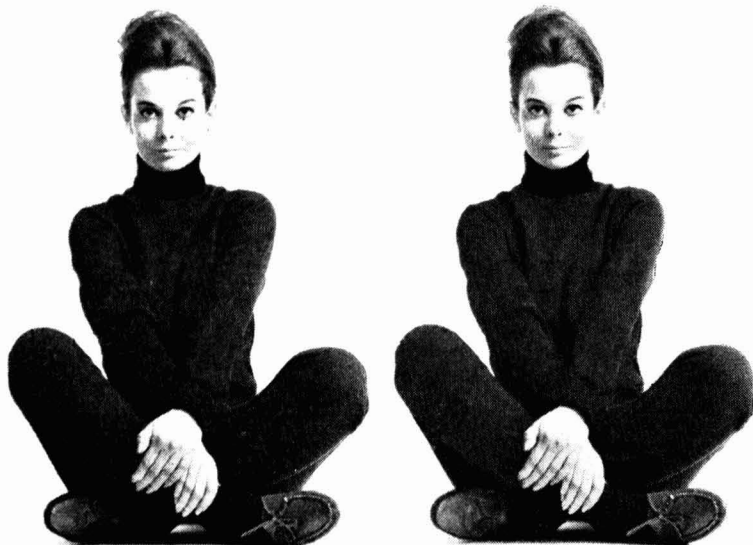
in fact, all that the name **NUODEX**  
implies in quality, consistency and service

*PS. Do any of your products lose Drying power on storage? NUAGE PASTE will combat this without hastening initial Dry or altering ultimate film properties. Send for leaflet and sample to*

Sole Distributors:

**DURHAM RAW MATERIALS LTD.**  
**1/4 GT. TOWER ST., LONDON, E.C.3.**

MANsion House 4333



**You know the advantages of "two-pack" urethanes?**



**Well, Daltosec 158 has them in one**

And the same goes for Daltosec 258. Two new urethane moisture-curing prepolymers from ICI with the same high order of drying speed, resistance and durability as 'two-pack' urethane compositions, without the disadvantage of two-pack materials. Compatible with each other in any proportion, to give lacquers with a wide gradation of properties.

X511

**From Daltosec 158**  
giving soft, flexible films for  
rubber, plastics, paper.

**To Daltosec 258**  
giving films of great hardness  
for wood finishing.

**Imperial Chemical Industries Ltd**  
London SW1 England





**NEW**

### **MICRODOL SUPER**

meets the requirements of the industry for constantly more finely ground extenders.

It combines great fineness with low oil absorption and makes it possible to formulate semi gloss and gloss paints at higher PVC

*—Please ask for our technical bulletins and for further information.*

# **100% NORWEGIAN TALC**

**BERGEN - NORWAY**

U. K. Representatives:  
**H. A. Watson & Co. Ltd.,**  
448, Derby House,  
Exchange Buildings, Liverpool, 2.





the widest  
range  
of epoxies  
for paint

# Araldite

liquid resins solid resins  
solutions specialities  
curing agents

may we send you detailed information?

C I B A

CIBA (A.R.L.) Limited, Duxford, Cambridge, Tel. Sawston 2121. Araldite is a registered trademark.

# Who makes the best metallic finishes?



# You-with Alcoa Tinting Pastes

Today, automobile manufacturers and buyers, prefer the tough metallic finishes that highlight the best in modern styling, and keep looking beautiful for years.

For the last 15 years, Aluminum Company of America (Alcoa) has supplied the bulk of the aluminium pigment for automotive finishes in the United States. Alcoa does not make paint. But it does make a comprehensive line of aluminium pigments that make it easier for you to produce these best-quality, best-selling aluminium pigmented paints.

Working in close co-operation with manufacturers of automotive finishes, Alcoa has developed a wide variety of Tinting Pastes. Rigid control of particle size eliminates both oversized flakes (which cause seeding) and fine colloidal aluminium (which spoils colour). As a result, you can take maximum advantage of the new colour pigments and synthetic resins to produce strikingly beautiful polychromatic pastel finishes.

Send the coupon below for more information, or for samples of Alcoa Tinting Pastes. And, remember, we also have a full range of aluminium pastes and powders for other formulations. Alcoa International, S.A., Avenue d'Ouchy 61, Lausanne, Switzerland. (A subsidiary of Aluminum Company of America.)



To: Imperial Aluminium Company Limited, Kynoch Works, PO Box 216, Witton, Birmingham. Please send technical literature, samples of Alcoa pigments and quotations to:

Name .....

Company .....

Position .....

Address .....

.....

JOC 2



As yet, the chemical in this laboratory mock-up is commercially unborn. But like so many substances formulated by DCL in experimental quantities, it may be tomorrow's Bisol chemical in world demand. DCL have all the facilities to offer customers product research assistance, and to scale-up pilot plant output to tonnage production. DCL supplies chemicals in bulk, in drum, or 'specials' by the gallon.

**THE DISTILLERS COMPANY LIMITED • CHEMICALS & PLASTICS GROUP**

Bisol Sales Office • Devonshire House • Piccadilly • London W1  
(MAYfair 8867)

chemicals at speed, in bulk or drum



ALCOHOLS • KETONES • PLASTICISERS  
ESTERS • MONOMERS • ORGANIC ACIDS

chemical  
eye view

tomorrow  
in  
embryo

# WHO MAKES PAINTS SPREAD BETTER, SOAPS CLEAN BETTER, LOTIONS FEEL SMOOTHER?



**Cyanamid does**

Does it with AEROSOL\* Surface Active Agents. Through their detergent, dispersing, foaming and emulsifying powers, these versatile chemicals endow scores of products with more desirable properties. They are especially valuable in emulsion polymerization. Cosmetics, paints, polishes, detergents, plastic films are just a few products which benefit from AEROSOL Surfactants. Five outstanding grades are: AEROSOL 18, 22, and TR 70, OT 75, OT 100. *Who makes good products even better?* Cyanamid does.

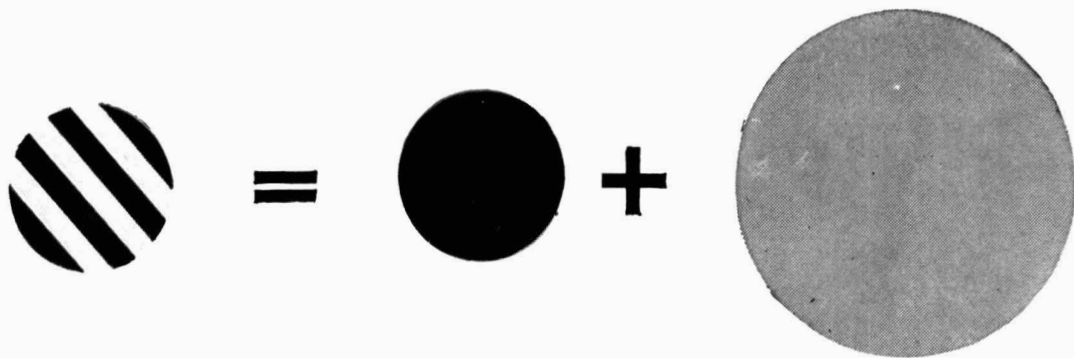
**\*Trademark**

write to:

**CYANAMID OF GREAT BRITAIN LIMITED**



GENERAL CHEMICALS DIVISION · BUSH HOUSE · ALDWYCH · LONDON WC2



The drying power of 1 part of

**cozirc 69**

equals or excels that of

1 part of cobalt naphthenate 6%

plus .

2½ parts of lead naphthenate 24%

and costs less!

**cozirc 69**

LEAD FREE · LOW VISCOSITY · LOW ODOUR

hardman and holden ltd  
manchester 10





**"You think this is a tough film!  
you just wait until you see  
what Vandike Emulsion can do"**

Yes, Vandike copolymer and homopolymer emulsions give a really tough film. Combined with adhesion, weathering, durability, excellent tinting characteristics and other properties essential to paint quality. Through research, British Oxygen works both to maintain this quality and develop new products and processes for the future. Our technical service is always at your disposal. And we deliver either in drums or by tanker.





## TIOXIDE

white pigments for beautiful colours

TIOXIDE titanium pigments are opaque and brilliantly white. Their performance gives unequalled standards of quality in paints for industrial and all decorative finishes.

BTP, the largest producer of titanium pigments in Europe, is selling in over 70 countries and has plants in England at Billingham and Grimsby and in Australia, Canada and South Africa.

**British Titan Products Co Ltd**

I47-4B

10 STRATTON STREET LONDON W.1

## INDEX OF ADVERTISERS

<b>A</b>	
Alcoa International .. .. .	viii, ix
<b>B</b>	
Badische Anilin- & Soda-Fabrik AG .. .. .	Cover
Beck, Koller & Co. (England) Ltd. .. .. .	xxv
British Oxygen Chemicals Ltd. .. .. .	xiii
British Titan Products Co. Ltd. .. .. .	xiv
BX Plastics Ltd. .. .. .	xxiv
<b>C</b>	
Ciba (ARL) Ltd. .. .. .	vii
Cory, Horace, & Co. Ltd. .. .. .	Cover
Crosfield, Joseph, & Sons Ltd. .. .. .	xxix
Croxton & Garry Ltd. .. .. .	xix
Cyanamid of Great Britain Ltd. .. .. .	xi
<b>D</b>	
Distillers Co. Ltd., The .. .. .	x
Dunlop Chemical Co. Ltd. .. .. .	xxxix
Durham Raw Materials Ltd. .. .. .	iv
<b>E</b>	
Esso Petroleum Co. Ltd. .. .. .	i
<b>G</b>	
Golden Valley Colours Ltd. .. .. .	xxii
<b>H</b>	
Hardman & Holden Ltd. .. .. .	xii
Hercules Powder Co. Ltd. .. .. .	xvi
Heydon, Harold, & Co. Ltd. .. .. .	Cover
Hoechst Chemicals Ltd. .. .. .	xxxii
<b>I</b>	
ICI Ltd. (Dyestuffs Division) .. .. .	v
<b>K</b>	
Kronos Titanium Pigments Ltd. .. .. .	iii
<b>L</b>	
Laporte Titanium Ltd. .. .. .	xxi
Lonabarc Ltd. .. .. .	xxxiv
<b>M</b>	
Metchim & Son Ltd. .. .. .	xxxv
Mitchell, W. A., & Smith Ltd. .. .. .	xxxiv
<b>N</b>	
Norwegian Talc AS .. .. .	vi
<b>P</b>	
Paint Trade Benevolent Fund .. .. .	xx
<b>R</b>	
Resinous Chemicals Ltd. .. .. .	xxvi
<b>S</b>	
Shell Chemical Co. Ltd. .. .. .	xxx
Steel, J. M., & Co. Ltd. .. .. .	xxxiii
<b>V</b>	
Vickers-Armstrongs (Engineers) Ltd. .. .. .	xxvii
Vinyl Products Ltd. .. .. .	xxiii
<b>W</b>	
Wilkins Instrument Research AG .. .. .	xviii
<b>Y</b>	
Younghusband Stephens & Co. Ltd. .. .. .	ii

## JOURNAL OF THE OIL &amp; COLOUR CHEMISTS' ASSOCIATION

Vol. 47 No. 10 October 1964

MEMBER OF THE  
AUDIT BUREAU  
OF CIRCULATIONS

Publications Committee

- D. S. Newton, A.M.C.T., C.G.I.A. (Hon. Editor)  
 J. E. Arnold, B.SC., PH.D., F.R.I.C., A.INST.P.  
 B. N. Auld, B.SC.  
 D. W. Berryman, A.S.A.S.M., A.R.A.C.I.  
 I. C. R. Bews, B.SC., A.R.I.C.  
 A. Blenkinsop  
 R. D. Calvert, B.SC., A.R.I.C.  
 V. T. Crowl, B.SC., PH.D., D.I.C., A.R.C.S., F.R.I.C.  
 G. P. Cryer, B.SC.  
 J. A. L. Hawkey  
 D. M. James, B.SC., F.R.I.C.  
 K. L. Jones  
 L. Jones, B.SC.  
 W. F. McDonnell, A.R.I.C., A.M.B.I.M.  
 A. McLean, B.SC., A.R.T.C., F.R.I.C.  
 A. T. S. Rudram  
 W. A. Rutherford, F.R.I.C.  
 L. R. Seaborne  
 F. Sowerbutts, B.SC.TECH.  
 L. Tasker, B.SC.  
 L. J. Watkinson, M.SC., PH.D., A.R.I.C.  
 G. Whitelaw  
 T. Whitfield  
 P. Wilson

Editorial correspondence should be addressed to the Hon. Editor, *JOCCA*, Monmouth House, Almondsbury, Near Bristol.

General correspondence should be addressed to :

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

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

Assistant Secretary : P. R. Davis, F.C.C.S.,  
 F.C.A., A.T.I.I.

Assistant Editor : G. R. Heaford, B.SC.

Annual subscription to non-members £5 in UK, £6 abroad, post free, payable in advance. Single copies : 10s. in UK, 12s. abroad, post free.





# HERCULES

## New from Hercules Dresinol 303

*An aqueous resin dispersion  
compatible with natural and  
synthetic latices.*

The need existed. Industry sought an emulsion, or dispersion, of a stable, neutral resin which was really resistant to ageing. It was vital that the dispersion should be free from organic solvents and blend readily with either natural or synthetic rubber latex. For use in adhesives, it had to impart the intense grab, tack and tenacity which is expected of rosin derivatives. It had to be pale in colour, and stay so. So Hercules developed Dresinol 303. Does it fill the bill? We certainly believe so. Dresinol 303 is in commercial production in the U.K. now. May we send you details?

**HERCULES POWDER COMPANY LIMITED**

ONE GREAT CUMBERLAND PLACE, LONDON W.1. Telephone: AMBassador 7766

# JOURNAL OF THE OIL & COLOUR CHEMISTS' ASSOCIATION

Vol. 47

OCTOBER 1964

No. 10

## TRANSACTIONS AND COMMUNICATIONS

### Water Thinnable Alkyd Media\*

By R. A. BRETT

Paint Research Station, Waldegrave Road, Teddington, Middlesex

#### Summary

*Studies on the chemistry of water thinnable alkyd media are described in four parts—(a) structural factors affecting the solubility of maleinised oils and non-oil modified alkyds in aqueous bases including some general film properties of these materials as one-component systems, (b) the effect of alkyd structure and type of water soluble melamine on some film properties of mixed alkyd/amino-resin systems, (c) the mechanism of curing of these two-component systems dealing particularly with the rate of loss of volatile base on stoving and the role of the amino-condensate in forming cross-linked polymer, and (d) problems, such as poor storage stability, anomalous viscosity reduction behaviour and "cratering" tendency, that may be encountered with the alkyd/melamine system in practice.*

#### Véhicules Alkyds Pour Délégage à l'eau

#### Résumé

*Diverses études portant sur la chimie des véhicules alkyds pour délégage à l'eau sont détaillées en quatre points—(a) facteurs structuraux affectant la solubilité des huiles malléinisées et les alkyds modifiés non-huileux dans les bases aqueuses, y compris quelques propriétés pelliculaires générales de ces substances en tant que systèmes à composant unique ; (b) l'effet de la mélamine soluble dans l'eau de type et de structure alkyd sur quelques propriétés pelliculaires de systèmes composés d'un mélange alkyd/amino-résineux ; (c) le procédé de cuisson de ces systèmes à deux composants, traitant particulièrement du taux de perte de base volatile lors de l'étuvage et du rôle de l'amino-condensation dans la formation de polymère et (d) divers problèmes, tels que la faible stabilité en conservation, la diminution anormale de la viscosité et la tendance aux "cratères" problèmes qui, dans la pratique, peuvent être rencontrés lorsqu'il s'agit du système alkyd/mélamine.*

#### Alkydharze, die mit Wasser Verdünnt Werden Können

#### Zusammenfassung

*In vier Abschnitten wird das chemische Verhalten von Alkydharzen untersucht, die mit Wasser verdünnt werden können. (a) Strukturelle Faktoren, die Löslichkeit maleinierter Ole und nicht-ölgiger modifizierter Alkydharze auf wässriger Basis beeinflussen—die filmbildenden Eigenschaften dieser Stoffe in einem "Einkomponenten-System"; (b) die Auswirkungen der Alkydstruktur und der Art des wasserlöslichen Melamins auf verschiedene filmbildende Eigenschaften einer Alkyd-Aminoharz-Mischung; (c) die Vorgänge beim Trocknen dieser "Zweikomponenten-Systeme" unter Berücksichtigung des Verlusts an flüchtiger Basis beim Einbrennen sowie der Rolle der Aminokondensate bei der Bildung von Polymerisaten mit Querverbindungen; (d) verschiedene andere Probleme, wie z. B. schlechte Lagerungsfähigkeit, ungewöhnliches Viskositätsverhalten und die Neigung zur "Kraterbildung", die bei der praktischen Verwendung von Alkyd-Melamin-Mischungen auftreten.*

\*Presented to the Newcastle Section 2 January 1964, London Section 15 January 1964, and West Riding Section 10 March 1964.

## INTRODUCTION

Over the last few years a fairly extensive programme of work has been carried out at the Paint Research Station under the general heading of water thinnable media. Both emulsion and water soluble systems have been studied in this programme, but the present paper deals specifically with water soluble alkyd resins of the type suitable for use in stoving compositions.

For convenience in this paper, the term "alkyd" has been used in its broadest sense, covering any polyester based on polyhydric alcohols and polybasic acids with or without modifying long chain monobasic fatty acids (saturated or unsaturated) or triglyceride oils. Within this broad classification it is thus permissible to include simple maleinised oils, since they contain the specified ingredients, although structurally rather different from conventional oil modified alkyd resins of the phthalic anhydride type.

The work will be described broadly under four headings :

- I. The alkyd component—particularly dealing with structural features that are conducive to good solubility characteristics and film properties ;
- II. Alkyd/amino resin systems—indicating various combinations that can be used particularly with alkyds based on trimellitic anhydride ;
- III. The mechanism of curing of alkyd/amino-resin systems ; and
- IV. Some problems encountered in their general usage.

## PART I

## THE "ALKYD" COMPONENT

**Maleinised Oils—Solubility in Ammonia**

These are a well established class of water soluble coating materials and the work has been mainly concerned with studies on the reactions occurring between maleic anhydride and the drying oil during processing and in particular the loss of acidity that is encountered during this reaction. This loss in acid groups is shown by appreciably lower acid and saponification values of the maleinised products than would be expected if all the potential acid groups of the maleic anhydride were fully available.

The general method of preparation is to react the drying oil with just sufficient maleic anhydride to render the product soluble in dilute ammonium hydroxide, or other volatile bases, thereby allowing a high proportion of the original reactivity of the drying oil to be retained in the product for the building of coherent and water-resistant polymeric structures during the subsequent drying process (whether air drying or stoving). Any loss of acidity during the maleinisation is, therefore, of direct interest, since it might require the use of a high proportion of maleic anhydride to ensure solubility, the reactivity of the oil thereby being unduly reduced.

In work at the Paint Research Station it was found that low acid and saponification values were obtained not only with non-conjugated oils, e.g. linseed oil (maleinised at 200°C), but also with a conjugated oil, e.g. tung oil, maleinised at a much lower temperature (80°C).



From studies with model compounds such as methyl sorbate (the simplest conjugated ester) it was established that this loss of acidity between  $C_{18}$  conjugated esters and maleic anhydride involved essentially two factors—one associated with resistance of the adducts to hydrolysis and the other with the loss of potential acid groups by chemical reaction. Direct addition between an anhydride ring and a reactive methylene group present in the adduct to form a keto-acid could account for the permanent loss of acidity. This type of reaction has been mentioned tentatively in the literature<sup>1</sup> as a possible mechanism to account for the acidity lost during the maleinisation of non-conjugated esters.

It was also found that, when fumaric acid was used to modify tung oil instead of maleic anhydride, then, although a higher reaction temperature was needed (about 180°C) for a reasonable rate of reaction, the full acidity in the reaction product was realised, enabling solubility in ammonium hydroxide to be achieved where equivalent amounts of maleic anhydride were insufficient for this purpose.

However, with linseed oil, fumaric acid did not appear to offer any significant advantages over maleic anhydride in terms of acid and saponification values, possibly due to partial conversation to the anhydride at the higher temperatures needed (220°C) for reaction.

Typical results illustrating these features are shown in Table I.

TABLE I

CHARACTERISTICS OF DRYING OILS MODIFIED WITH MALEIC ANHYDRIDE AND FUMARIC ACID

Product composition (by wt.)	Reaction temp. °C	Solubility in dilute $NH_4OH$	Acid value (calcd.)	Acid* value (found) mg KOH/g	Saponification value (calcd.)	Saponification value (found)
Tung oil : maleic anhydride(85 : 15)	80	Soluble	172	94	331	260
Tung oil : maleic anhydride(90 : 10)	80	Disperses	115	67	283	240
Tung oil : maleic anhydride (95 : 5)	80	Insoluble	57	41	235	216
Tung oil : fumaric acid (95 : 5.9) ..	180	Soluble	57	56	233	233
Linseed oil : maleic anhydride(80 : 20)	220	Soluble	229	159	379	325
Linseed oil : fumaric acid (80 : 23.7) ..	220	Soluble	221	167	365	301

\*Aqueous acetone solvent titrated with aq. KOH.

### Non-oil modified Alkyds—Factors Affecting Solubility in Aqueous Bases

It was felt that in terms of both speed of cure and subsequent film performance the best results with water soluble alkyds were likely to be obtained with systems

which had been taken to as high a degree of reaction as possible, i.e. those in which a minimum of carboxyl groups were retained to ensure solubility in an aqueous base. Therefore a brief study was made of the ways in which the degree of reaction of an alkyd could be increased whilst still maintaining the solubility requirements.

Three approaches were made :

#### *Effect of Ether Groups*

Long chain polyethers have been used for preparing water dispersible air drying oil modified alkyds<sup>2</sup>. Completely soluble polyesters can, however, be readily prepared having either linear or branched structures.

*In Linear Systems* : Although alkyds of the straight chain type prepared from saturated components would not be expected to yield cross-linked films on stoving, they provide a convenient system for demonstrating the effect of the introduction of ether groups into the polymer chain on solubility characteristics under aqueous conditions.

The solubility of a selection of such alkyds esterified to approximately the same acid value is shown in Table II. The results clearly indicate the marked improvement in solubility possible with the hydrophilic ether group.

TABLE II  
SOLUBILITY OF LINEAR ALKYDS IN DILUTE AMMONIA

System	Acid value (mg KOH/°)	Solubility in dilute ammonia
Adipic/ethylene glycol .. .. .	62	Insoluble
Adipic/diethylene .. .. .	63	Fairly readily soluble
Adipic/polyethylene glycol (M. Wt. 400) ..	64	Readily soluble
Succinic acid/ethylene glycol .. .. .	62	Insoluble
Succinic acid/polyethylene glycol (M. Wt. 400)	61	Readily soluble

*In Branched Systems* : In a formulation containing glycerol as a major ingredient, thus :

#### *Alkyd A*

4.5 mols phthalic anhydride  
1.0 mol adipic acid  
3.66 mols glycerol  
1.5 mols glycol

the use of a glycol containing one or more ether groups has a marked effect on solubility as the results in Table III show.

TABLE III  
SOLUBILITY OF BRANCHED ALKYDS OF THE ALKYD A\* TYPE IN DILUTE AMMONIA

Glycol used	Acid value (mg KOH/g)	Percentage degree of esterification	Solubility in aqueous ammonia
1, 2 propylene glycol .. ..	58	87	Insoluble
Diethylene glycol .. ..	56	87	Soluble (slight cloudiness)
Triethylene glycol .. ..	46	89	Soluble

\*Mol. ratio 4.5/1.0/3.66/1.5.

In this series diethylene glycol had a relatively small effect on solubility, but triethylene glycol had a pronounced effect and enabled a lower acid value (higher degree of esterification) to be achieved whilst still retaining solubility. The amount of triethylene glycol used was equivalent to the introduction of 3.5 per cent by weight of ether oxygen, an indication of the strong hydrophilic nature of this grouping.

#### *Effect of Alcohols of High Functionality*

Pentaerythritol and dipentaerythritol were used as examples of high functionality alcohols and their effect on the solubility characteristics of alkyd A examined by suitable substitution of the alcohol components as shown in Table IV.

TABLE IV  
SOLUBILITY IN DILUTE AMMONIA OF ALKYDS OF THE ALKYD A TYPE CONTAINING HIGH FUNCTIONALITY ALCOHOLS

Polyhydric alcohols	Molar* ratio	Acid value (mg KOH/g)	Percentage degree of esterification	Solubility in aqueous ammonia
Glycerol/1, 2 propylene glycol ..	3.66 : 1.5	58	87	Insoluble
Pentaerythritol/1, 2 propylene glycol	1.4 : 4.2	54	88	Soluble
Dipentaerythritol/1, 2 propylene glycol .. ..	0.46 : 5.62	51	88	Soluble

\*Molar ratios calculated to give polyol mixtures of the same overall effective functionality.

These results indicated that slightly improved solubility characteristics could be obtained with the higher functional alcohols. To meet the functionality requirements, however, a high proportion of dihydric alcohol had been included in the formulation. This, from theoretical considerations, would be expected to lead to a broadening of the molecular weight distribution in the final product and may be the reason for the improvement in solubility noted by virtue of mutual solubility effects. With dipentaerythritol there would of course be the added effect of the introduction of a small proportion of ether groups

(0.5 per cent by wt.), which may have made some contribution to the improvement in solubility that was found.

### *Effect of Acids of High Functionality*

Trimellitic anhydride and pyromellitic acid (having functionalities 3 and 4 respectively) were used as examples of high functionality acids. These acids were used in conjunction with adipic acid, the relative amounts of each acid being adjusted to maintain the same overall effective functionality as that of alkyd *A*. Their effect on water solubility characteristics is shown in Table V.

TABLE V  
SOLUBILITY IN DILUTE AMMONIA OF ALKYDS OF THE ALKYD *A* CONTAINING HIGH FUNCTIONALITY ACIDS

Polybasic acids	Molar ratio	Acid value (mg KOH/g)	Percentage degree of esterification	Solubility in aqueous ammonia
Phthalic/adipic (alkyd <i>A</i> ) .. ..	4.5 : 1	58	87	Insoluble
Trimellitic/adipic* .. ..	3 : 1	50	89	Readily soluble
Pyromellitic/adipic* .. ..	0.345 : 1	27	94	Soluble

\*In these alkyds propylene glycol (7 mols) was the only polyol used.

These results showed that with high functionality acids, products readily soluble in aqueous ammonia could be obtained even at relatively high degrees of reaction.

The reasons for this are probably twofold :

(a) A wider molecular weight distribution due to the use of a large proportion of dihydric alcohol in the formulation to maintain the functionality requirements, and

(b) A different distribution of free carboxyl groups among the molecular species than is obtained with phthalic anhydride type alkyds.

Thus, one would expect that with trimellitic anhydride, due to its extra carboxyl group, quite high molecular weight compounds could be built up with a relatively high proportion of free carboxyl groups along the polymer chains, so enhancing solubility.

To see whether this was the case in practice, fractionation studies have been carried out on simple trimellitic and phthalic type polyesters.

The results from these experiments clearly demonstrated that trimellitic anhydride was giving a more efficient distribution of  $-\text{COOH}$  groups in the sense that a greater proportion was found in the high molecular weight fractions than in the phthalic anhydride polyester. Thus by using trimellitic anhydride the most difficult components of the alkyd to solubilise (i.e. the high molecular weight material) are provided with a relatively high proportion of carboxyl groups to effect easier solubility.

This difference in distribution can be represented diagrammatically as shown in Fig. 1, where *P* represents phthalic anhydride, *G* glycerol, *T* trimellitic anhydride, and *E* ethylene glycol.

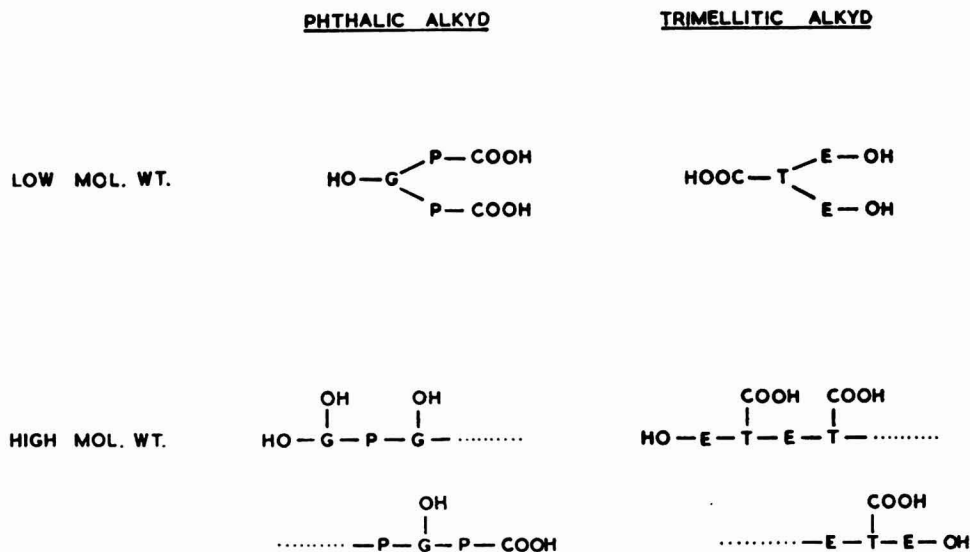


FIG. 1. DIAGRAMMATIC REPRESENTATION OF ALKYD STRUCTURE

The type of carboxyl distribution obtained with trimellitic anhydride (and presumably also with pyromellitic acid) may thus be the primary reason for the efficiency with which these highly functional acids promote water solubility.

### Stoving of Alkyd Films

#### *Maleinised Oils*

Normal systems of this type are reactive towards atmospheric oxygen and will cure by oxidation/polymerisation reactions at stoving temperatures of about 120°C in the presence of metal driers to give hard, tough, glossy films.

Thus it has been found that even a simple maleinised linseed oil film stoved for 45 minutes at this temperature gave a reasonably good performance as a one- or two-coat system on mild steel. Better performance ratings, however, can be obtained by using linseed/tung oil mixtures, and in particular a combination of linseed and tung oil with cyclopentadiene, which was then maleinised to give an ammonia soluble product, gave very promising results.

However, all these systems suffer from one main disadvantage, that of poor initial colour due to yellowing, whether the films are stoved at 120°C or allowed to dry at room temperature. This severe yellowing is the inevitable result of exposing an oxidised drying oil type system to the vapours of a volatile nitrogenous base—ammonia or tertiary bases all have the same effect and such interactions form the basis of an accelerated yellowing test. Hence these water soluble oils are usually limited in their application to primer coatings or to the darker coloured finishes.

In order to keep a good initial colour in stoved films it is necessary to keep the oxidisable components in volatile base-solubilised systems to a minimum and preferably use none at all.

### *Non-oil Modified Alkyds*

Non-oil modified alkyds of the type described above can be used as one component stoving compositions to give films of very good initial colour. Since these materials are not oxygen reactive, an alternative means of cross-linking the film is required and this is done by stoving at a temperature high enough to remove essentially all the volatile base, so releasing the carboxyl groups and enabling an esterification reaction to proceed with the free hydroxyl groups. This esterification reaction only occurs at an appreciable rate above 180°C and hence this type of coating would be limited to situations where such high stoving temperatures could be tolerated.

From observations on the stoving of various types of non-oil modified alkyds at high temperatures, it was clear that the trimellitic type gave the best all round properties combining after stoving for half an hour at 200°C both extreme hardness with excellent flexibility.

Thus the general principle of using a trifunctional acid to give good solubility to an alkyd system at high degrees of reaction appeared to be justified from the performance of the stoved films.

At the present time, however, trimellitic anhydride is not readily available in large quantities and other trifunctional aromatic acids are difficult to manufacture.

It is possible, however, to make high functionality acids *in situ* by reacting maleic anhydride or fumaric acid with unsaturated fatty acids, preferably of the conjugated type, and then building up an oil modified alkyd type water soluble material on the product. Such an approach would be expected to lead to dried films of rather poor initial colour due to the reasons mentioned above, but some compromise should be possible and by suitable choice of the fatty acids and degree of maleinisation to arrive at a system which would cure at a reasonably low temperature without discoloring too badly.

So far only one-component systems have been considered. The next section deals with the alkyd in combination with amino-resin condensates.

## PART II

### ALKYD RESIN/AMINO-CONDENSATE SYSTEMS

In order to reduce the temperature needed to cure water soluble alkyd films that contain no drying oil modification, it is normal practice to make use of a second component such as a reactive water soluble phenolic or amino-resin condensate. By this means chemical reactions other than simple esterification can be brought into play at temperatures as low as 120°C to give effective curing of the film.

In this part of the paper a study of the effects of some variations in alkyd structure on the film performance of stoved alkyd/amino condensate systems is described. Clearly the number of possible combinations and permutations of this two-component mixture are endless and some restriction on the range of materials examined had to be made.

Since it had been found in the previous work that the use of highly functional acids, such as trimellitic anhydride, had a beneficial effect both on solubility



and on some film properties, studies with the alkyd/amino-condensate mixtures were confined to alkyds containing this anhydride as one of their main ingredients.

Numerous formulations can of course be devised based on trimellitic anhydride. In general, however, to offset the high functionality of this acid and prevent premature gelation, a large proportion of the polyhydric alcohol must be no more than difunctional. This means that changes in alkyd structure introduced by variations in type of polyol will be restricted to those containing two hydroxyl groups.

Some formulations used in this work were based on those reported in the literature<sup>3, 4</sup>, but some novel variations were introduced to examine special features of alkyd structure or to improve particular film properties.

Three general types of trimellitic alkyds were examined: (i) trimellitic anhydride/adipic acid/diol combinations, (ii) similar to (i), but containing capric acid (C<sub>10</sub>) as modifying agent, and (iii) castor oil modified trimellitic alkyds.

The water soluble amino-condensates used were of the melamine type—a considerable amount of the earlier work being done with a partially methoxylated trimethylol melamine. More recently a methoxy ethanol modified melamine has been developed and still more recently fully methoxylated methyl melamines of high purity have been prepared in the laboratory for evaluation.

#### **Trimellitic Anhydride/Adipic Acid/Diol Type Alkyds**

The physical properties of films of this alkyd in conjunction with a water soluble partially methoxylated melamine condensate, particularly with regard to hardness and flexibility, can be varied over quite a wide range by altering the molar ratio of trimellitic to adipic acid in the starting formulation. Thus a relatively high trimellitic to adipic molar ratio (say 3 : 1) gives rather hard brittle film, whereas with adipic in excess, soft films are obtained. The best compromise seems to be approximately 1 : 1 or 3 : 2 mols of trimellitic to adipic acid.

Several diols were tried, notably 1, 2 propylene glycol, diethylene glycol and neopentyl glycol. Flexibility of the final film could be improved by using diethylene glycol instead of propylene glycol, but neopentyl glycol gave alkyds having better wetting characteristics for glass and aluminium substrates and was therefore preferred.

Some typical film properties of an alkyd prepared from 3 mols trimellitic anhydride, 2 mols adipic acid, 8 mols neopentyl glycol (excess hydroxyl = 23 per cent) and solubilised in aqueous trimethylamine (just sufficient base being added to neutralise the free acidity, AV = 54 mg KOH/g) are given below in Table VI, the alkyd being cross-linked with varying amounts of a partially methoxylated melamine condensate.

These results showed that although adequate water resistance could be obtained at high levels of melamine addition, this was only achieved at the expense of flexibility. An interesting feature was that the amount of cross-linked

TABLE VI  
STOVING OF A TRIMELLITIC/ADIPIC ALKYD WITH VARYING AMOUNTS OF A PARTIALLY METHOXYLATED MELAMINE CONDENSATE

Melamine percentage addition* by wt.	Stoving conditions temp./time	MEK inextractable (%)	Flexibility (mandrel bend test)	Water resistance (24 hrs. cold immersion)
15	120/30 mins.	55	Passed 7-8	Poor
25	120/30 „	67	„ 6-7	Good
40	120/30 „	76	„ 3	Good
15	150/10 „	56	„ 8	Poor
25	150/10 „	69	„ 6	Moderate

\*On alkyd solids.

material formed (as assessed from MEK inextractable figures)† was very similar for the same amount of melamine condensate whether stoving had been carried out at 120/30 minutes or 150/10 minutes.

#### Capric Acid Modified Trimellitic Alkyds

The introduction of capric acid into water soluble alkyds was found to improve the wetting characteristics of such alkyds for glass and aluminium surfaces. Furthermore the use of this fatty acid did not cause any discoloration of the film when stoved at temperatures up to 150°C.

A suitable formulation was 3 mols trimellitic anhydride, 1 mol capric acid, 0.5 mol adipic acid, 6.25 mols diethylene glycol (excess hydroxyl=13.5 per cent).

At an AV of 47, this alkyd was very close to gelation, but still completely soluble in aqueous trimethylamine at 50 per cent solids. Film properties on stoving with different amounts of a partially methoxylated melamine are given in Table VII.

TABLE VII  
STOVING OF A CAPRIC MODIFIED TRIMELLITIC ALKYD WITH A PARTIALLY METHOXYLATED MELAMINE AT 120°C FOR 30 MINUTES

Melamine condensate percentage addition* by weight	MEK inextractable (%)	Flexibility (mandrel bend test)	Water resistance (24 hrs. cold immersion)
10	67	Passed 9	Poor
15	72	„ 9	Moderate
20	85	„ 8	Good

\*On alkyd solids.

†The MEK inextractable content quoted throughout this paper is obtained by hot Soxhlet extraction of the stoved film for four hours with MEK, drying to constant weight under vacuum and recording the weight of residue as a percentage of the original film weight.

In this series a better compromise between adequate flexibility and water resistance was obtained. Thus the alkyd with 20 per cent melamine resin added gave good water resistance with reasonable flexibility, a considerable degree of cross-linking being achieved as indicated by the high MEK inextractable figure.

### Castor Oil Modified Trimellitic Alkyds

Castor oil/phthalic anhydride alkyds are well established as components of solvent thinned industrial alkyd/melamine systems and it was of interest to see whether their water thinnable counterparts based on trimellitic acid had any particular merit.

It was found that castor oil modified trimellitic alkyds could be made in one heating operation, initial cloudiness in the original reaction mixture gradually clearing as esterification proceeded. A typical formulation was as follows: 3 mols trimellitic anhydride, 0.67 mols castor oil, 5.5 mols diethylene glycol (excess hydroxyl=36 per cent).

The "oil-length" of this alkyd was approximately 37 per cent, rather lower than that used with conventional castor/phthalic systems. The alkyd at an AV of 34 was completely soluble in aqueous trimethylamine at 50 per cent solids. The solution was mixed with 10, 15, 20, 30 and 40 per cent water soluble melamine resin (by weight on alkyd solids) and stoved at 120°C for half an hour.

Films stoved on both glass and aluminium showed particularly good wetting for the substrate, as had been found with the capric modified system. Some properties of the stoved films are given in Table VIII.

TABLE VIII

STOVING OF A CASTOR OIL MODIFIED TRIMELLITIC ALKYD WITH A PARTIALLY METHOXYLATED MELAMINE AT 120°C FOR 30 MINUTES

Melamine condensate percentage addition* by weight	MEK inextractable (%)	Flexibility (mandrel bend test)	Water resistance (24 hrs. cold immersion)
10	55	Passed 9	Poor
15	68	„ 9	Moderate
20	73	„ 9	Moderate
30	78	„ 5	Moderate
40	80	„ 4	Fairly good

\*On alkyd solids.

The water resistance of this series was rather worse than that found with the capric modified alkyds, although good flexibility was possible with a relatively high degree of cross-linking in the film.

The general conclusion at this stage of the work was that a water soluble partially methoxylated melamine resin was not a suitable cross-linking agent for alkyds of the trimellitic type, difficulties being encountered in attaining

adequate flexibility and water resistance in the same film, only a compromise between these two properties being possible.

### Modified Melamine/Formaldehyde Condensates

From a number of model experiments it was concluded that if a longer chain modification of the melamine resin could be made, whilst still retaining its water solubility, better results in terms of flexibility of stoved films might be obtained. A modification with butyl alcohol was not, of course, possible since water solubility would be lost, but by using 2-methoxy ethanol, an alcohol of about the same chain length as butanol, this difficulty could be overcome.

A methoxy ethanol-modified melamine resin (Fig. 2) prepared in the laboratory was compared with the normal methylated melamine as cross-linking agent for various trimellitic alkyds. As anticipated there was a significant increase in flexibility of the stoved film, a reasonably high degree of water resistance being maintained.

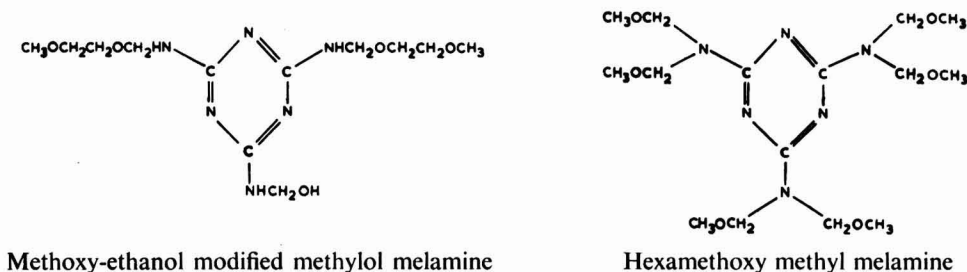


FIG. 2. WATER SOLUBLE MODIFIED M/F CONDENSATES

Recently a fully methoxylated water soluble melamine condensate has been evaluated as a cross-linking agent for water soluble alkyds of the trimellitic type<sup>5</sup>. This condensate, hexamethoxy methyl melamine, is a crystalline material and is fairly readily prepared in the laboratory in a pure state<sup>6</sup>.

It will be noted from Fig. 2 that since hexamethoxy methyl melamine is a fully etherified methylol melamine, it does not, of course, contain any active or replaceable hydrogen atoms as with the previous partially etherified melamine condensates. This fundamental difference in structure shows up dramatically in the type of film obtained on heating the resin alone. Thus the partially methoxylated or the methoxy ethanol modified melamine give very hard films on heating alone for say half an hour at 120°C, the partially methoxylated film being particularly brittle. With hexamethoxy methyl melamine, on the other hand, no appreciable self-curing occurs, i.e. a liquid film is obtained, unless a strong acid, such as phosphoric or hydrochloric acid, is present to catalyse a curing reaction.

This difference in reactivity enables a harder type of alkyd resin to be used in conjunction with the fully methoxylated melamine and still retain good flexibility. In Table IX results for a partially methoxylated and a fully methoxylated melamine/alkyd system are given demonstrating this effect.

TABLE IX

STOVING OF TRIMELLITIC/ADIPIC ALKYDS WITH MELAMINE CONDENSATES AT 120°C FOR 30 MINUTES

System	Trimellitic adipic molar ratio	MEK inextractable (%)	Flexibility (mandrel bend test)	Water resistance (24 hrs. cold immersion)
Alkyd <i>A</i> + 20% PM ..	3 : 1	65	Failed 1	Good
„ <i>A</i> + 20% HM ..	3 : 1	69	Passed 9	V. good
„ <i>A</i> + 30% HM ..	3 : 1	85	„ 9	„
Alkyd <i>B</i> + 25% PM ..	3 : 2	67	Passed 6-7	Good
„ <i>B</i> + 25% HM ..	3 : 2	76	„ 9	„
„ <i>B</i> + 30% HM ..	3 : 2	78	„ 9	V. good
„ <i>B</i> + 40% HM ..	3 : 2	78	„ 9	„

PM = partially methoxylated melamine condensate.

HM = hexamethoxylated melamine condensate.

Alkyd *A* above represents the hard type of alkyd and as can be seen from the results the fully methoxylated melamine enables films of excellent flexibility and high MEK inextractable content to be obtained, unlike films cross-linked with the partially methoxylated type. Similar, although not so dramatic, effects are noted with alkyd *B*. Very good water resistance was also possible with hexamethoxylated melamine condensate cross-linked films.

### PART III

#### THE MECHANISM OF CURING OF ALKYD/AMINO-RESIN SYSTEMS

It has been fairly well established<sup>7, 8</sup> that in the case of *solvent* soluble alkyd/butylated amino resin systems, the main curing reaction during stoving is the etherification of free hydroxyl groups of the alkyd with the methylol or butoxy groups of the amino resin resulting in the loss of water or butanol respectively.

Earlier work at the Paint Research Station also indicated that such etherification reactions were catalysed by the presence of carboxyl groups<sup>9</sup>, e.g. by the free acidity present in the alkyd. In subsequent work it was found from radio-chemical studies using C<sub>14</sub> labelled stearic acid that there was strong evidence for a *direct* reaction between the carboxyl group and the amino resin during stoving at 120°C. Confirmation of the possibility of this direct esterification reaction was a fact published recently by workers<sup>10</sup> in the United States in studies on the reaction of an acrylic acid copolymer with a melamine/formaldehyde condensate. Using model compounds, the presence of methylene ester bridges was established after heating the system at 150°C with or without the presence of an acid catalyst.

These observations, therefore, underline the importance of free carboxyl groups in initiating cross-linking reactions during the stoving of alkyd/amino resin compositions.

With *water soluble* systems there is, of course, one essential difference from the solvent type, and that is the availability of the carboxyl group—this being normally neutralised by a volatile organic base in order to obtain initial water solubility. It is, therefore, of interest to know how quickly this volatile base would be lost during the initial stages of stoving so releasing the carboxyl groups and enabling them to play their part in the curing reaction. It is also of interest to have some idea of how much base is left behind after a normal stoving period. A significant amount might, of course, affect the subsequent film performance.

### Rate of Loss of Volatile Base on Stoving

The most convenient way of studying the rate of loss of base on stoving is by determining the nitrogen content of the films at intervals. This is obviously not so straightforward when an amino resin is present due to its own high nitrogen content. In order to avoid this complication, simple solutions of the alkyds alone were studied.

In the first series of experiments a range of trimellitic type alkyds were examined as solutions in ammonia and trimethylamine, films (approximately  $37\mu$  dry thickness) being analysed for nitrogen content by a micro-Kjeldahl technique after stoving for 30 minutes at  $120^\circ\text{C}$ . A laboratory prepared maleinised linseed oil dissolved in aqueous ammonia and stoved for 45 minutes at  $120^\circ\text{C}$  was also examined. Very little hardening of the alkyd films took place under these stoving conditions, the temperature being too low for any appreciable esterification. With the maleinised oil, however, fully cured films were obtained, oxidation/polymerisation reactions taking place readily under the conditions used. The results are shown in Table X.

TABLE X  
NITROGEN CONTENTS OF ALKYD AND MALEINISED OIL FILMS STOVED AT  $120^\circ\text{C}$

Type of medium	Acid value	Viscosity (50% solids) in aqueous base. Poises	Solubilising base	Original nitrogen (%)	Nitrogen lost (%)
Trimellitic/capric alkyd ..	57	3.5	$(\text{CH}_3)_3\text{N}$	1.64	100
"    "    "    ..	57	4	$\text{NH}_3$	1.54	95
Trimellitic/adipic alkyd ..	57	>200	$(\text{CH}_3)_3\text{N}$	1.40	64
"    "    "    ..	57	>200	$\text{NH}_3$	1.24	61
Maleinised linseed oil + 0.1% manganese ..	—	2	$\text{NH}_3$	4.78	78



The results showed that with a relatively low viscosity alkyd virtually all the nitrogen was lost on stoving with both ammonia and trimethylamine as solubilising agents. With the higher viscosity alkyds and the maleinised linseed oil, which would increase in viscosity on stoving due to oxidation/polymerisation reactions, a significant amount of nitrogen remained in the film.

Ammonium salts of carboxylic acids can decompose on heating according to the following schemes :



Under aqueous stoving conditions reaction (1) would be expected to predominate. This is substantiated by the results obtained with the low viscosity alkyd which showed almost complete loss of nitrogen in half an hour at 120°C. The significant amounts of nitrogen remaining in the film with the more viscous alkyd or maleinised oil solubilised with ammonia could be caused by :

(a) A restriction of the volatilisation of  $\text{NH}_3$ , particularly from the lower layers of the film, so throwing the equilibrium in favour of ammonium salt, and/or

(b) The partial conversion of ammonium salts into non-volatile amides.

A second series of experiments demonstrated that probably (a) was the major cause, there being evidence for only small amounts of amide formation with a high viscosity alkyd solution in ammonia. With alkyds solubilised in a tertiary base, e.g. trimethylamine, no simple amide formation is, of course, likely.

In this second series of experiments, the rate of loss of ammonia from alkyd films was compared with that of trimethylamine, triethylamine and 2-dimethylamino ethanol on stoving at 120°C. Attempts were also made to establish whether the residual base could be completely removed from the film on prolonged stoving.

A high viscosity type of alkyd based on trimellitic anhydride adipic acid and neopentyl glycol was used. This type of alkyd had shown the highest retention of base in the previous experiments and would probably be closest in behaviour to an alkyd stoved in the presence of amino resin as would be the case in practice.

Just sufficient of each base was added to the alkyd to neutralise the free acidity and the solids reduced to 50 per cent by the additions of distilled water. Films approximately 37 $\mu$  thick were applied to glass panels and their nitrogen contents determined after various periods of stoving at 120°C.

Results are plotted graphically in Figs. 3 and 4 as nitrogen loss (per cent) from films against stoving time.

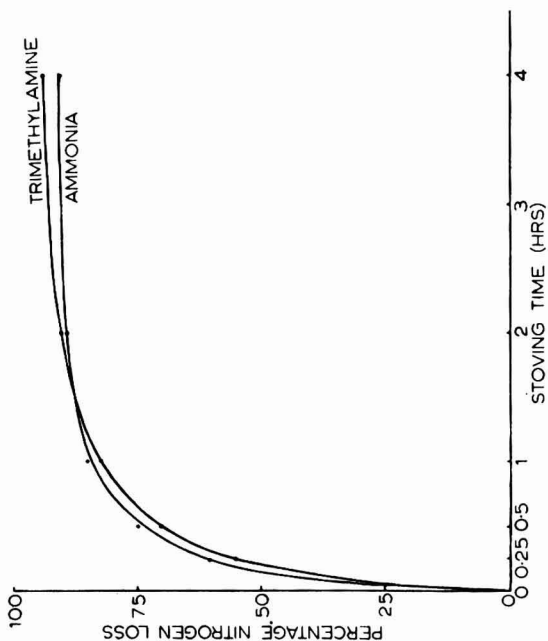


FIG. 4. NITROGEN LOSSES FROM FILMS OF A TRIMELLITIC/ADIPIC/NEOPENTYL GLYCOL TYPE ALKYD DISSOLVED IN AQUEOUS MEDIA ON STOVING FOR FOUR HOURS AT 120°C

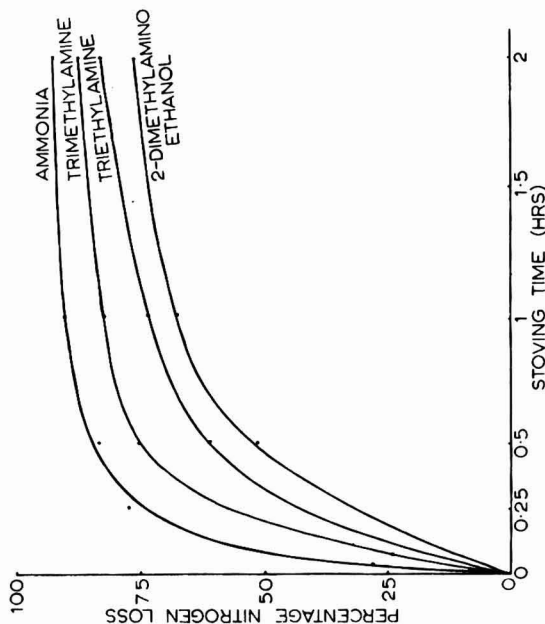


FIG. 3. NITROGEN LOSSES FROM FILMS OF A TRIMELLITIC/ADIPIC/NEOPENTYL GLYCOL TYPE ALKYD DISSOLVED IN AQUEOUS MEDIA ON STOVING AT 120°C

From Fig. 3 it is evident that all the bases examined are evolved fairly quickly in the early stages of stoving—ammonia, trimethylamine and triethylamine being released approximately in order of molecular weight. With 2-dimethylamino ethanol, however, the rate was lower than would be expected from its molecular weight, due presumably to association through its hydroxyl groups.

With ammonia and trimethylamine between 25 and 35 per cent of base were lost in the first five minutes, corresponding to release of approximately 30 per cent of the original acidity of the alkyd. Thus for an original acid value of 50 just neutralised with base, an acid content equivalent to 15 mg KOH/g after five minutes' stoving would be available to promote the curing reaction with amino-condensate.

After a half to one hour's heating (a typical stoving schedule for an alkyd/melamine resin condensate) significant amounts of base were left in the films, this being particularly marked with 2-dimethylamino ethanol.

On further stoving, up to two hours the rate of loss of ammonia appeared to be very low indeed, whereas with the other bases appreciable amounts were being evolved.

In Fig. 4 the results from even longer stoving periods are given for a similar type of alkyd, solubilised with ammonia and trimethylamine. In the initial stages again a slightly higher rate of loss of ammonia compared with trimethylamine was found. The rate of loss of ammonia after  $1\frac{1}{2}$ -2 hours then levelled out as before, but in this case was overtaken by the loss of trimethylamine. These results suggested that in the alkyd film solubilised with ammonia a small amount of nitrogen was being held through some chemical reaction possibly amide formation by the dehydration of an ammonium salt (reaction (2) above). With the trimethylamine solubilised system, however, such a reaction was not likely to occur, so that this amine was being lost slowly all the time.

Although these results apply only to simple alkyd solutions, one can make a few predictions about the likely behaviour of the system when stoved in the presence of amino-condensate.

First, there would seem to be no reason why the volatile base should not be lost from the system as readily as with the simple alkyd solutions in the very early stages of stoving, so that initial curing promoted by the release of some free acid should be unaffected. The amount of base retained by the film after a normal stoving schedule, however, would probably be greater than with simple alkyd solutions, due to rapid hardening as curing proceeds.

With ammonia, of course, there would be the added complication of the possibility of some amide formation—as indicated from long-term experiments. Such amides, however, are not necessarily detrimental since they may react with the amino-condensate and so become integrated with the high molecular weight portion of the film.

The figures for residual nitrogen content over normal stoving periods suggest that as much as 50 per cent of the volatile base might be retained by the film when amino-condensate is present.

Clearly a more accurate measurement of the rate of loss of volatile base from the combined alkyd/amino condensate system during curing would be of interest.

### The Role of the Amino-Resin Component

To obtain information on the extent to which the amino-resin component became incorporated with the highly cross-linked material of the film during curing, stoved films were divided into methyl ethyl ketone (MEK) inextractable and extractable portions and the nitrogen content of each determined. A feature which complicated this technique was, of course, the fact that some of the residual nitrogen found would come from the solubilising agent used—trimethylamine in this case. However, the figures for retained base in simple alkyd solutions suggested that the amount of nitrogen arising from this source would be relatively small compared with that from the amino-resin, particularly in view of the vacuum treatment used to remove residual MEK.

All the films examined were stoved on glass at 120°C for half an hour and extracted hot by refluxing with MEK in a Soxhlet apparatus for five hours. Solvent was removed from the inextractable portion under vacuum (1 mm) and from the soluble portion by distillation followed by the same vacuum treatment. Nitrogen contents of the residues so obtained were then determined using a micro-Kjeldahl technique.

Results obtained in this manner with a water soluble urea/formaldehyde condensate, a partially methoxylated melamine and a fully methoxylated melamine/formaldehyde condensate in combination with laboratory prepared trimellitic type alkyds are shown in Table XI.

TABLE XI

DISPOSITION OF NITROGEN IN MEK INEXTRACTABLE AND EXTRACTABLE PORTIONS OF STOVED TRIMELLITIC ALKYD/AMINO CONDENSATE FILMS

Ref.	Amino-condensate and amount added by wt.	MEK inextractable (%)	Percentage nitrogen found in :		Percentage nitrogen (in terms of total film) in :	
			Inextractable portion	Extractable portion	Inextractable portion	Extractable portion
A	Urea/formaldehyde 20 per cent	56	7.3	2.2	4.1	1.0
B <sub>1</sub>	Partially methoxylated melamine/formaldehyde 20 per cent	62	11.2	0.6	7.0	0.23
B <sub>2</sub>	„ „ 20 per cent	63	9.5	0.5	6.0	0.18
C	Hexamethoxylated melamine/formaldehyde 20 per cent	67	4.2	1.1	2.8	0.35

From the figures in Table XI some idea of the probable distribution of the three amino-condensates between the highly cross-linked portion of the film and the soluble portion can be obtained if the following assumptions are made : (i) that the amino-condensate itself has substantially the same nitrogen content in both the inextractable and extractable portions of the film, and (ii) that

no nitrogen-containing volatile material from the amino-condensate is lost during stoving or during the recovery of MEK from either portion of the film.

Bearing these assumptions in mind, the amount of amino-condensate in the cross-linked portion of the film and also the ratio of alkyd to amino-resin can be calculated, as shown in Table XII.

TABLE XII  
DISTRIBUTION OF AMINO-CONDENSATE IN STOVED FILMS (120°C/30 MINUTES) OF TRIMELLITIC ALKYDS

Ref.	Amino-condensate	Proportion of original amino-resin in MEK inextractable (%)	Alkyd/amino-resin† ratio in MEK inextractable (approx. by wt.)
A	Urea/formaldehyde .. .. .	80	2.9 : 1
B <sub>1</sub>	Partially methoxylated melamine/formaldehyde .. .. .	97	2.8 : 1
B <sub>2</sub>	.. .. .	97	2.8 : 1
C	Hexamethoxylated melamine/formaldehyde	89	4.0 : 1

†Original mixture was 5 : 1 (on solids).

These figures indicated that the partially methoxylated melamine/formaldehyde resin became almost fully integrated with the network structure on stoving. With the urea/formaldehyde condensate, on the other hand, only 80 per cent was active in the sense of forming or bringing about the formation of cross-linked polymer. The hexamethoxylated melamine/formaldehyde condensate, although falling between these results, involved a larger proportion of alkyd in the network structure, the ratio of alkyd and amino resin being 4 : 1 in this case compared with about 3 : 1 for the other condensates. This difference could be attributed to the reduced reactivity of the fully methoxylated melamine with itself (as mentioned in Part II), preferred reaction with the alkyd component occurring.

## PART IV

### PROBLEMS ENCOUNTERED IN THE USAGE OF WATER THINNABLE ALKYD-AMINO RESIN SYSTEMS

Current work is concerned with some of the problems that may be encountered in the handling of these water thinnable alkyd-amino resin systems, particular attention being given to storage stability, viscosity reduction behaviour and application defects.

#### Storage Stability

Water soluble stoving resins often show poor storage stability ; pH changes accompanied by clouding of the solution or even complete separation of the

resinous components can occur within a few weeks in the worst cases. Gloss changes in paints stored at different initial pH readings have been reported<sup>11</sup>.

Possible causes for instability with water soluble alkyd-amino resin systems can be summarised as follows :

- (i) Reaction between any free formaldehyde in the amino-condensate with the base solubilised alkyd component regenerating free acid—only likely to be serious if ammonia is used as a volatile base.
- (ii) Reaction between the alkyd and amino resin—i.e. a slow curing at room temperature.
- (iii) Reaction of the amino resin with itself—i.e. a slow self-cure.
- (iv) Hydrolysis of the ester groups in the alkyd, so releasing free hydroxyl and carboxyl groups, the latter lowering the pH and leading to an increased chance of (ii) and (iii) above by a catalytic action.
- (v) Aminolysis of ester groups by excess base—this is only likely with ammonia, primary or secondary amines and would lead to the formation of fragments of polymers terminated with amide or hydroxyl groups.
- (vi) Loss of volatile base by evaporation, the carboxyl terminated polymers so liberated being precipitated or catalysing reactions (ii) and (iii).

In order to reduce the number of factors involved in studying this problem, the amino-condensate portion of the system was withheld, the examination being restricted to the alkyd component alone dissolved in aqueous base. The number of ways in which storage instability could arise was therefore restricted to possibilities (iv), (v) and (vi).

However, by ensuring that no substantial loss by volatilisation occurred (control experiments confirmed this) and by using a tertiary base (to eliminate aminolysis reactions), the number of factors could be reduced essentially to one—namely (iv)—the ease with which the ester groups of the alkyds could be hydrolysed under conditions of mild alkalinity as provided by the aqueous nitrogenous base.

Preliminary studies have been carried out with simple linear polyesters and in one series, using phthalic anhydride with a range of different glycols, the following structural features were examined in relation to storage stability as assessed from pH drop, development of cloudiness and viscosity change :

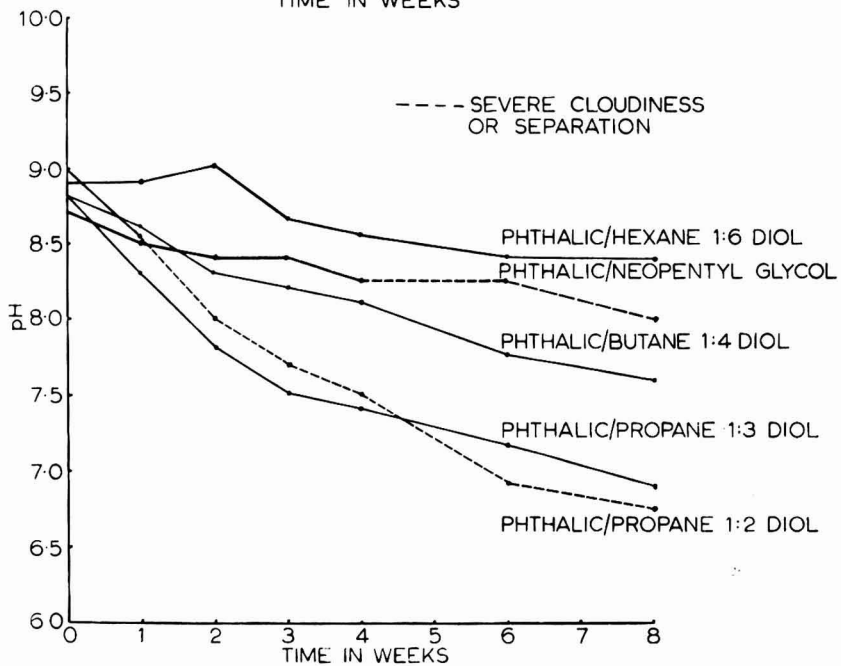
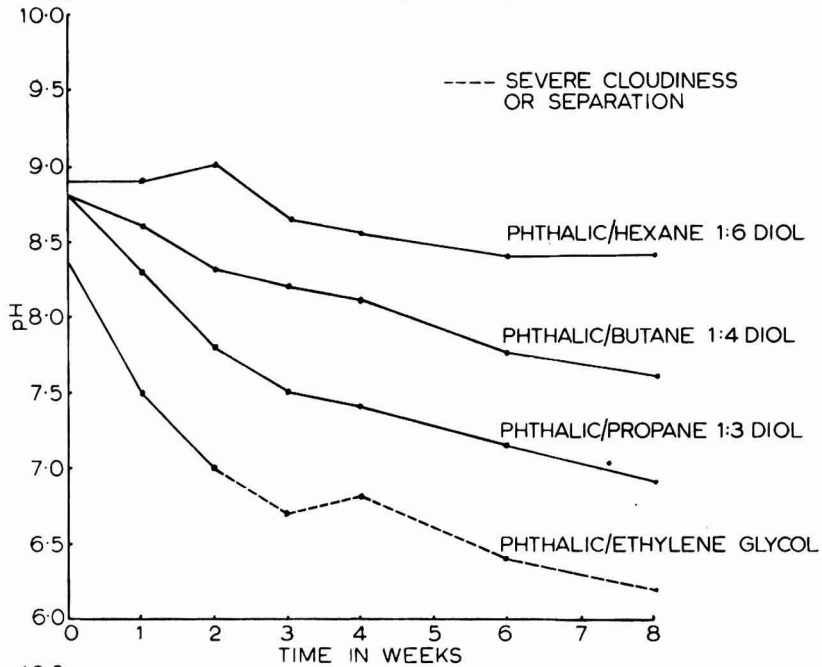
(a) The effect of molecular weight of glycol used—this, for a given dibasic acid, will determine the number of ester groups per unit weight of polyester. In other words for a given solids content of polyester, the concentration of ester linkages would decrease with increasing chain length of glycol used, and it was of interest to see whether the concentration of ester groups altered in this way was directly related to the pH change.

(b) Effect of type of hydroxyl groups in the diol, i.e. whether of primary or secondary type. This could be examined directly, keeping ester concentration constant for a given weight of polyester by comparing 1, 2 with 1, 3 propane diol as starting material.



(c) Possible shielding effects of alkyl branches in a polyol, such as the methyl groups in neopentyl glycol, on adjacent ester groups.

Some typical observations made on pH changes are illustrated in Figs. 5 and 6.



FIGS. 5 AND 6. pH CHANGES OF SOLUTIONS OF PHTHALIC ANHYDRIDE POLYESTERS ON STORAGE AT 25°C IN AQUEOUS 2-DIMETHYLAMINO ETHANOL

The conclusions reached so far can be summarised as follows :

(1) The amount of hydrolysis occurring appears to be directly proportional to the concentration of ester groups per unit weight of polyester in the case of linear polyester chains. Thus at a given solids content, polyesters prepared from long chain diols were the best in terms of steadiness of pH. No abnormal effects were noted when ester groups were attached to adjacent carbon atoms, e.g. as with ethane diol.

(2) Polyesters prepared from a diol having two primary hydroxy groups were slightly better than from one having a primary and a secondary hydroxyl group in terms of both pH constancy and development of cloudiness.

(3) There was no evidence for any substantial shielding effects arising from the methyl side chains in neopentyl glycol. This glycol behaved in the same way as would have been expected from a  $C_5$  straight chain glycol.

### Viscosity Reduction Behaviour

Anomalous viscosity dilution characteristics are shown by various types of water soluble media<sup>12, 13</sup>, although the use of alcohol/water solvent mixtures as diluents tends to give smoother dilution curves<sup>14</sup>. With most alkyds, for example, a characteristic feature is the sudden drop in viscosity which occurs at a certain critical solids content. Reducing with water down to this critical value may in fact follow a fairly normal viscosity reduction pattern. Sometimes, however, the approach to this critical point passes through a stage where the viscosity actually increases on dilution with water.

The behaviour of some laboratory prepared and commercial water soluble resins on dilution with water is shown in Fig. 7.

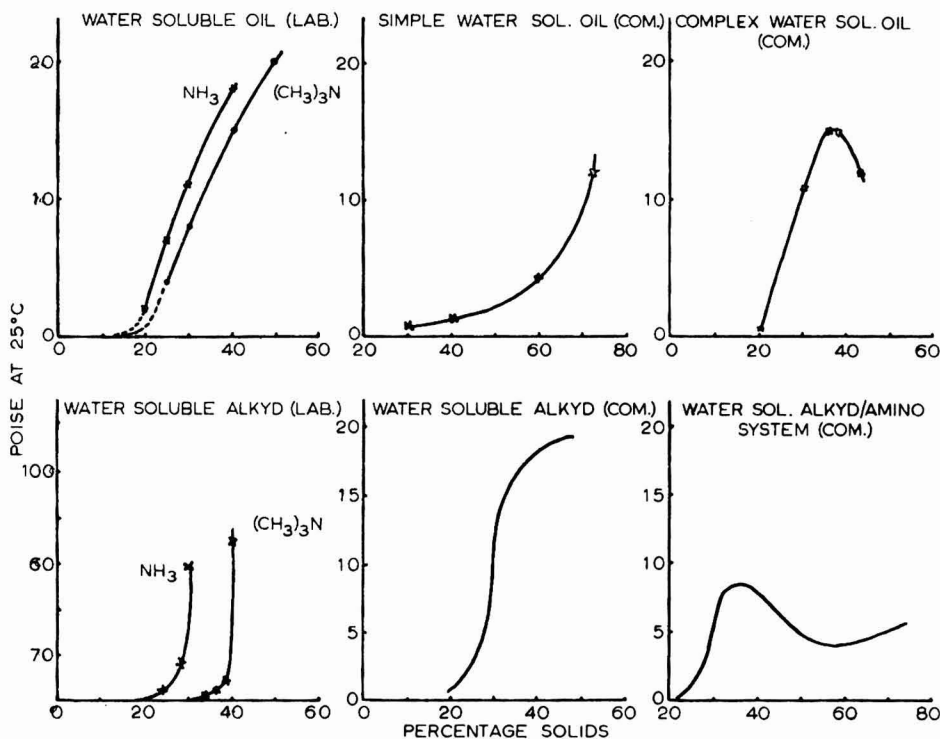


FIG. 7. TYPICAL VISCOSITY/DILUTION CURVES FOR COMMERCIAL (COM.) AND LABORATORY (LAB.) PREPARED WATER SOLUBLE SYSTEMS

Clearly, a better understanding of the nature of aqueous solutions of water soluble resins is required before any explanations can be offered for the anomalies found on diluting these materials.

As a first step in this work, it was felt that a polyester system should be found which would not only reproduce the type of anomalies shown in Fig. 5, but also be structurally much simpler than conventional water soluble systems. Then a more systematic study could be made of the effect of changes in this structure on viscosity characteristics and possibly some clues as to the nature of the polymer when in solution would become apparent.

A series of different types of polyesters were, therefore, examined and it was found that linear polyesters based on adipic acid and neopentyl glycol could be prepared which gave viscosity dilution curves in aqueous bases showing most of the characteristics obtained with the more complex water soluble alkyd systems.

Viscosity/dilution curves of two samples of an adipic/neopentyl polyester taken to different degrees of reaction are shown in Figs. 8 and 9.

Fig. 8 shows a typical "hump" in the water dilution curve with a sudden drop at approximately 45 per cent solids concentration. Dilution of the original polyester with methyl ethyl ketone gives a smooth viscosity/concentration relationship. In Fig. 9 the dilution curves of a similar polyester but of slightly higher average molecular weight reproduced the viscosity inversion phenomenon that was noted with some maleinised oils and alkyd/amino systems. This polyester was not completely soluble in aqueous ammonia, aqueous trimethylamine being required to maintain solution on diluting in this case. Again dilution of the original polyester with MEK gave a smooth viscosity/concentration relationship.

A feature of this model system is that it can only contain three types of molecules, namely: hydroxyl terminated, carboxyl terminated and those containing a carboxyl at one end and a hydroxyl at the other, the relative amounts of each being determined by the initial hydroxyl excess used and the degree of esterification achieved.

A detailed examination of the effects of the composition of this linear polyester on its viscosity characteristics is being carried out and a few interesting observations have already been made:

- (a) Solely hydroxyl terminated molecules even of relatively low molecular weight can give rise to anomalous viscosity characteristics when added to a "normal polyester." Solely carboxyl terminated molecules, on the other hand, have better solution properties and anomalous behaviour only occurs with the higher molecular weight species.
- (b) The introduction of branching into the linear polyester system improved both solubility and dilution characteristics. This was probably caused by the more even distribution of carboxyl groups brought about by the use of a trifunctional acid.

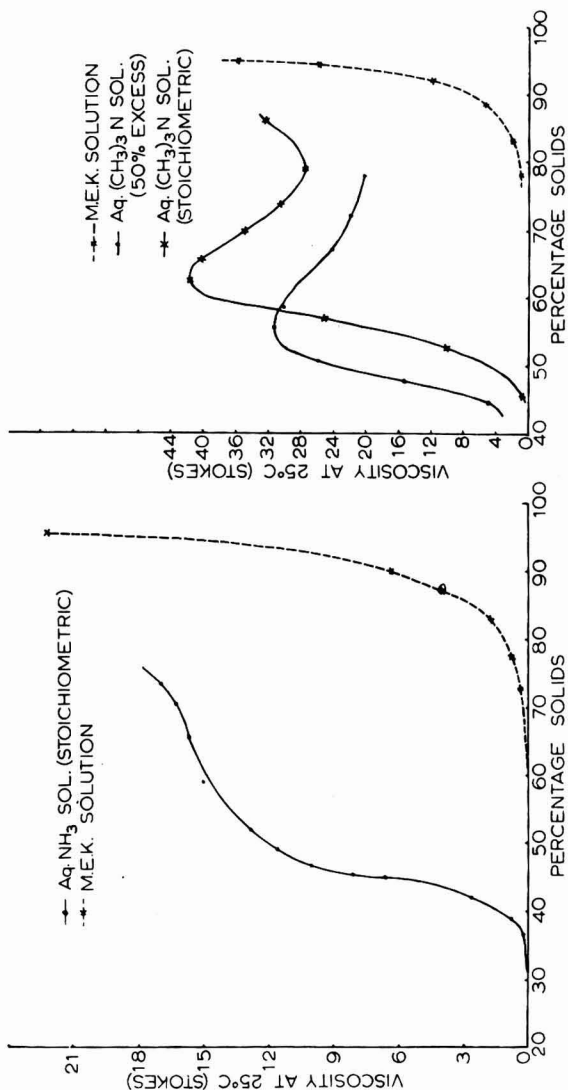


FIG. 8. VISCOSITY/DILUTION CURVES OF ADIPIC/NEOPENTYL POLYESTER ACID VALUE 57

FIG. 9. VISCOSITY/DILUTION CURVES OF ADIPIC/NEOPENTYL POLYESTER ACID VALUE 49

(c) A viscosity/concentration curve obtained by concentrating the solution stepwise gave very much the same result as that obtained by diluting the system in the conventional manner. This, at least, shows the reversibility of the phenomenon.

Insufficient information is available as yet to understand fully the behaviour of these materials on dilution. However, it seems certain that in the case of linear polyesters some form of molecular association essentially involving the hydroxyl terminated molecules is responsible for the enhanced viscosity observed at certain dilutions. Such behaviour can occur on diluting solvent soluble alkyds with a poor solvent and is thus not peculiar to aqueous systems. Furthermore, a closer examination of both solvent and water thinned systems

at a dilution corresponding to a point on the anomalous portion of the curve showed evidence for a non-Newtonian behaviour. This supports the idea of molecular association, but more work needs to be done on this aspect of the problem, and also on the reasons for the sudden drop in viscosity which occurs at higher dilutions.

### Application Defects

Water thinnable alkyd/amino resin systems often show application defects which can be classified generally into three main types: (i) Defects arising on initial application—e.g. the commonly described “crawling” or “cissing” phenomenon due to poor wetting of the substrate by the liquid paint film. This has been attributed to the abnormally high surface tension of water compared with the critical surface tension of common substrates<sup>15</sup>, (ii) Defects appearing during the early stages of stoving—e.g. the development of large pinholes or saucer-shaped depressions in the film, sometimes termed “cratering,” and (iii) Other defects which appear in the film during stoving—e.g. the production of tiny blisters or small pinholes, particularly at thick edges, due to the entrapment of air or water vapour bubbles within the film as the viscosity of the coating increases.

Work has been concerned with the second type of defect—namely cratering.

Examination under the microscope of stoved alkyd varnish films showed that this defect was invariably associated with a small lump of solid matter at the centre of the crater, and also that within this crater a very thin film of clear film still remained on the substrate. These features distinguish this defect from the one described as “cissing,” in which no lumps of solid material are normally present, and no residual film remains within the hole.

In Figs. 10 and 11 photographs of the crater-type defect are shown.

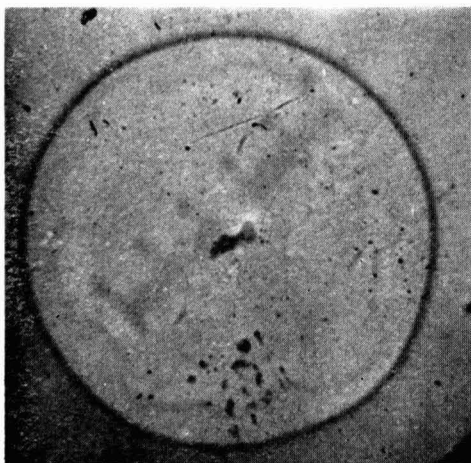


FIG. 10. A TYPICAL CRATER FORMED IN A WATER SOLUBLE ALKYD FILM ON STOVING AT 120°C

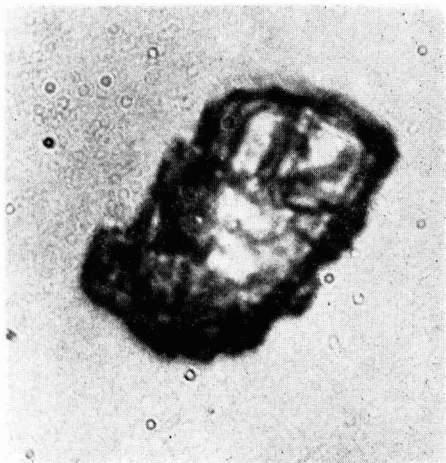


FIG. 11. A SOLID LUMP OF GELLED MATERIAL IN THE MIDDLE OF A CRATER

Work on the problem has been concerned with the following aspects :

- (a) The effect of different additives, such as wetting agents, high boiling solvents and excess base,
- (b) The effect of dust particles, and
- (c) The effect of removal of any gelled particles from the original resin.

### *Observations*

In the particular system studied it was found that the addition of small amounts of solvents such as benzyl alcohol and ethyl lactate had beneficial effects. Also a non-ionic surfactant gave some improvement. The addition of excess base, trimethylamine in this case, was, however, deleterious.

With regard to the question of dust particles, it was found that working in a dust-free cabinet generally reduced, but did not eliminate, the defect. From experiments in which controlled amounts of dust particles of a given size were allowed to contaminate the film, the extent of cratering did not follow regularly the amount of contamination, although generally increasing with increased contamination.

Finally, it was found that the removal of gelled particles by centrifuging or filtration followed by stoving in a dust-free cabinet improved the film appearance, but did not completely eliminate cratering.

### *Mechanism*

The phenomenon of cratering does not seem to be directly related to stresses set up by surface tension changes at the medium/substrate interface (the presence of a thin film within the crater still attached to the substrate suggests this), but more likely to stresses set up within the film itself as the result of preferential loss of base from the film surface leading to a more rapid cure in the upper layers. This process might also be considered as the development of poor wetting of the lower layers of the film by the upper, and hence one can then explain the beneficial effects of some solvents and wetting agents when used as additives.

The precise role of the solid particles in the formation of craters is not clear. These particles, from microscopic examination, appeared to be gel-like in nature, although, when dust was deliberately added, dust particles themselves were found to form a nucleus in the centre of the craters in some cases.

It is conceivable that the release of the stresses suggested above in the film is triggered off by the protuberance of a solid particle through the surface skin. The central position of the particle within the crater supports this contention.

These particles may be present in the original liquid medium, but can also be formed in the film during the stoving process. It would indeed be of interest to follow the birth of one of these craters photographically—the precise sequences of events could then be observed directly.

## CONCLUSIONS

From this work carried out on some aspects of the chemistry of water thinnable alkyd media, the main points of interest, taking each section in turn, would seem to be as follows :

(i) The maleinisation of conjugated oils led to a loss of acidity which may be attributed to two factors, one associated with resistance of adducts to hydrolysis and the other with loss of potential acid groups by chemical reaction. When fumaric acid was used to modify conjugated materials, significant acidity loss did not occur and solubility in aqueous ammonia was more readily achieved. With alkyd systems the presence of highly functional polybasic acids (e.g. trimellitic anhydride) was particularly effective in promoting good solubility at relatively high degrees of reaction. Film properties of some alkyds stoved at 200°C favoured the trimellitic type.

(ii) A simple evaluation of clear films of trimellitic alkyd mixed with a partially methoxylated melamine showed that the major problem was the simultaneous attainment of adequate flexibility and water resistance. With the fully methoxylated melamine condensate (i.e. hexamethoxymethyl melamine), the flexibility was particularly good possibly due to reduced reactivity of the melamine condensate with itself. A better compromise between water resistance and flexibility was possible.

(iii) By analogy with simple alkyd solutions, the loss of volatile base from alkyd/amino resin films on stoving at 120°C should be fairly rapid in the early stages so that initial curing promoted by free acid would be unaffected. The results suggested that over normal stoving periods as much as 50 per cent of the volatile base might be retained. Partially methoxylated melamine condensates became almost fully integrated with the cross-linked portion of the alkyd films. A fully methoxylated melamine, although not so completely reacted, involved a larger proportion of the alkyd in the network structure. This was again probably due to the reduced self-curing tendencies of the fully methoxylated condensate.

(iv) Preliminary studies on storage stability have shown that the pH of simple polyesters dropped quickly on storage in aqueous amine solutions. No abnormal effects were noticed when ester groups were attached to adjacent carbon atoms, but there was some evidence that ester groups based on secondary hydroxyls were more sensitive than those formed from primary hydroxyls. In studies on the viscosity dilution behaviour of linear polyesters (adipic acid/neopentyl glycol type), it was established that solely hydroxyl terminated molecules, even of relatively low molecular weight, could give rise to anomalous viscosity characteristics when added to a polyester solution having a normal viscosity/concentration curve. The enhanced viscosity found at certain dilutions was probably due to molecular association involving hydroxyl terminated polymers.

The "crater" type of film defect was invariably associated with a small lump of solid matter at its centre. It was possible that this solid material initiated crater formation by releasing stresses set up in the film resulting from more rapid curing in the upper surface. The incidence of this crater type of film defect was reduced by the use of small amounts of high boiling solvents such



as benzyl alcohol or ethyl lactate. No complete cure for this particular defect had, however, been found.

#### ACKNOWLEDGEMENTS

The author wishes to thank the Council and Director of the Research Association for granting permission to publish this paper and also his colleagues for their help in its preparation.

[Received 21 April 1964]

#### REFERENCES

1. Plimmer, H., *JOCCA*, 1949, **32**, 99.
2. Armitage, F., and Trace, L. G., *JOCCA*, 1957, **40**, 849.
3. Bolton, B. S., and van Strien, R. E., *Amer. Paint J.*, 1960, **44**, 71.
4. Wilkinson, R. F., *Off. Dig.*, 1963, **35**, 129.
5. Stephens, J. R., *Off. Dig.*, 1963, **35**, 380.
6. Englehardt, F., *et al*, *Kunst. Rundschau*, 1960, **7**, 433.
7. Wohnsiedler, H. P., *Am. Chem. Soc.*, New York Meeting, 1960, No. 20, 53.
8. Seidler, R., and Gratz, H. J., *Vith FATIPEC Congress*, 1962, 282.
9. Paint Research Station, Research Memorandum No. 297.
10. Saxon, R., and Daniel, J. H., *Am. Chem. Soc.*, Washington Meeting, 1962, No. 1, 277.
11. Phillips, G., *Paint Tech.*, 1962, **26**, 24.
12. Malyan, C. R., *Paint, Oil & Colour J.*, 1961, **140**, 412.
13. Hellens, F., *Paint Manuf.*, 1962, **32**, 231.
14. North, A. G., *JOCCA*, 1961, **44**, 119.
15. Fry, E. S. J., and Bunker, E. B., *JOCCA*, 1960, **43**, 640.

#### DISCUSSION AT LONDON SECTION

MR. A. R. H. TAWN asked what was meant by the term functionality in these condensation polymers, particularly in connection with the effect of carboxylic acids of high functionality on solubility. Various ratios of adipic, trimellitic and pyromellitic acid were used, and it was stated that the functionality was maintained constant. One could not make a mixture of trimellitic and adipic acids with a functionality of two, and so presumably Mr. Brett was referring to the functionality of the alkyd as a whole, i.e. by varying the COOH/OH ratio? Also no mention had been made of the effect of hydroxyl content of polyesters on their ease of solubility in water, as in his experience hydroxyl excess was the most important parameter which determined solubility.

MR. R. A. BRETT replied that concerning the last point, a separate study of the effects of hydroxyl content had not been made. This would certainly affect water solubility. The alkyds were in fact all made with the same hydroxyl excess, so that any side effects due to this factor would tend to be cancelled out. With regard to functionality, the term in this context really implied the overall effective functionality of the system. Alkyds of the same overall functionality should gel at the same degree of reaction and this was taken as a basis for comparing the effects of various structural features (such as those produced by polybasic acids) on solubility characteristics.

MR. N. R. FISK asked what was the range of sizes of the gel particles observed at the centres of the craters.

MR. BRETT said that some could be seen with the naked eye, and these were about a tenth of a millimetre in diameter.

MR. G. A. FISHER said that pinholes and craters had been said to be common; could Mr. Brett say which were the worst media?

MR. BRETT said that there were considerable variations. The worst were those based on a simple unmodified polyester. Introducing a long chain fatty acid reduced the tendency to form pinholes, but did not eliminate it.

MR. FISHER asked whether Mr. Brett would agree that the change from solvent systems to water-thinnables was a greater change than that from copal varnishes to alkyds.

MR. BRETT was in agreement. Changing the environment of the system was a major step and in any case a copal varnish could be considered as a type of alkyd.

MR. M. J. ZISSELL asked whether the presence or absence of a base would affect the mechanism of reaction between water soluble alkyd and amino resins.

MR. BRETT said that if the base were really strong, e.g. caustic potash, the cure would certainly be different. Triethylamine is said to give different results to trimethylamine, so the strength of the base may have some effect.

MR. ZISSELL asked how Mr. Brett would deal with the analysis of a mixture of alkyd, amino resin, and a volatile base.

MR. BRETT replied that he would send it to the analytical department! The analytical procedures that had been worked out were rather complex, and there was hardly time to go into them in detail.

MR. F. ARMITAGE said that the discovery of the solubility of maleinised oils in aqueous ammonia dated back to 1938, but it was only now that it was coming into common use in primers for automobile finishes, and for electrodeposition. It had been shown that part of the nitrogen remained in the resin on stoving, possibly forming amides or polyimides. Had such stoved films been examined applied (a) from solvents, and (b) from aqueous amine solution. Another point was whether there were differences between films on steel and on glass.

MR. BRETT replied that on the second point, the amount of nitrogen retained was unaffected by whether a steel or glass substrate was used. He had no results on a comparison of film performance from solvent or aqueous systems.

MR. ARMITAGE said that a temperature of 120°C had been quoted as the stoving temperature for maleinised oil, compared with 180°C for alkyds, but he would have thought that the optimum stoving temperature for maleinised oils was a little higher.

MR. BRETT replied that stoving took a little longer, about 45 minutes at 120°C, compared with 30 minutes for the alkyd.

MR. A. G. NORTH said that in the stoving system the evolution of about 30 per cent of base had been shown to occur in the first five minutes, and it was therefore suggested that the initial curing reaction would not be affected. In his experience, however, if 30 per cent of the base were lost the pH would still be about 7.8 and hence one would not expect an acid catalysed reaction to start.

MR. BRETT said that he had not measured the pH of the systems as the base content was reduced, but this would certainly be done. He felt, however, that with trimethylamine, the base used, a pH rather lower than that suggested would be obtained. A stronger base like triethylamine might, however, still give an alkaline environment.

MR. W. O. NUTT asked whether Mr. Brett had compared the incidence of cissing and cratering in water soluble alkyds with similar defects in ultra-low particle size acrylic and styrene latex systems, or with alkali-soluble vinyl acetate/maleic copolymers. Aqueous shellac solutions solubilised with ammonia can ciss and crater, but similar solutions made with triethanolamine were less susceptible.

MR. BRETT said that he had not so far studied this cratering with emulsion systems, but would bear this in mind.

MR. ZISSELL asked whether difficulties were experienced in measurement of the pH of pigmented water-soluble alkyds.

MR. BRETT replied that he had not yet examined pigmented systems.

MR. R. R. DAVIDSON asked why ammonia solubilised maleinised oils yellowed.

MR. BRETT said that normal yellowing at room temperature was thought to be due to the effect of atmospheric impurities, such as ammonia, on the oxidation products of drying oils. Thus in a standard yellowing test ammonia was used to accelerate yellowing of the dried film. On stoving maleinised oils the conditions were just right, therefore, to cause severe yellowing. Further work on yellowing was proceeding at the Paint Research Station.

MR. F. P. GRIMSHAW asked why hexamethoxy melamines were more effective than di- or tri-methoxymelamines in giving flexibility and water resistance in alkyd amino systems, in view of the low reactivity of the former and, presumably, the presence of free methoxy groups in the cured film. Was it a matter of compatibility with the alkyd.

MR. BRETT said that good flexibility was probably due to the high proportion of alkyd which became involved with a fully methoxylated melamine in the cross-linked portion of the film. This had been shown experimentally to be significantly higher than with a partially methoxylated melamine. The free methoxy content of the stoved films was not known, but may be lower than one might expect in view of the reasonable water resistance of these systems.

DR. P. A. TOSELAND asked whether Mr. Brett had experienced volatile bases evaporating before the solvent, thus causing precipitation of the alkyd. Would this be a possible cause of cratering, with the solid particles resulting from such precipitation.

MR. BRETT said that he had considered this as a possible cause of such defects. This could be why the addition of high boiling solvents improved matters.

MR. G. N. STOCKDALE said that Mr. Brett had forestalled his question by careful definition of terms, but many of the systems examined were not modified with a long chain fatty acid. Was it fair to call them alkyds, and had Mr. Brett any suggestions for a more explicit terminology.

MR. BRETT said that alkyd was a general term which had come to mean a number of things, and it might be better to call them polyesters. The systems examined were not oil modified in order to get a good colour on stoving.

MR. ARMITAGE asked what were the differences in performance between pyromellitic and trimellitic acids and wondered if the maleic adduct of sorbic acid had been considered as a raw material.

MR. BRETT said that pyromellitic acid, being tetrafunctional, tended to form gel particles during alkyd preparation, and so trimellitic acid was preferred. The maleic adduct of sorbic acid had not been used, but maleic adducts of longer chain acids, which were becoming commercially available, should be very useful in this field.

MR. J. R. BERRY, in proposing a vote of thanks to the speaker, said that it had been a pleasure to listen to such a well thought out lecture delivered in such a clear manner. The use of water soluble systems involved considerably more than merely turning on the tap, and he congratulated the author on his exposition of this very complex branch of technology.

## DISCUSSION AT NEWCASTLE SECTION

MR. J. BRAVEY asked for details of the mandrel and water-resistance tests, and whether tests had been done on pigmented resins.

MR. BRETT said the mandrel test was a simple bend test, done on films applied to 30 SWG aluminium. No. 9 corresponded to 10 per cent elongation of the film, a diameter of just under 0.125 in. The water-immersion test was for 24 hours, using an aluminium substrate, and was assessed by blistering. Pigmented films had been tested and followed the pattern of the clears.

MR. A. S. DEEKS asked whether maleic acid had been used to adduct with oils.

MR. BRETT said that it formed the anhydride when heated and therefore gave similar results.

MR. A. LAWS asked about the wetting properties for substrates of other water-soluble systems.

MR. BRETT replied that, in general, inclusion of long-chain fatty acids improved this property.

MR. FARROW said that a fair amount of solubilising base was left after stoving at 120°C, and asked whether higher temperatures had been used. The retained base would presumably affect subsequent coats.

MR. BRETT agreed, but said that no experiments had been done using higher temperatures.

MR. I. MAUGHAM said the manufacturers of hexamethoxymethyl-melamine advised stoving at 150°C, whereas 120°C had been used in these experiments. Also they deprecated the use of triethylamine.

MR. BRETT replied that, judging by the amount of MEK-inextractable, there was cross-linking at 120°C. He had noticed nothing special about triethylamine.

MR. A. LAWS asked about the effect of the solubilising base on substrate wetting.

MR. BRETT said excess trimethylamine was bad, and bases of lower volatility were better, but none gave a cure for cratering.

MR. J. BRAVEY asked when the craters appeared.

MR. BRETT said they usually appeared within one minute of any heat being applied ; and it was an interesting fact that the number per unit area was quite reproducible for any system.

MR. D. G. WALL had noticed a tendency for viscosities to drop on storage.

MR. BRETT said hydrolysis of ester groups would cause this, but a separation into two layers of different viscosity was common in his experience.

MR. K. BAXTER asked for the reason for the loss of acidity in making maleinised oils.

MR. BRETT said that, in addition to the resistance of anhydride groups to hydrolysis, it was thought there was a reaction causing loss of carboxyl groups by reaction with methylene groups in long-chain fatty acids, forming keto-acids.

MR. E. L. FARROW asked whether added solvents helped in wetting greasy surfaces, but Mr. Brett had not investigated this question.

## DISCUSSION AT WEST RIDING SECTION

DR. K. HARGREAVES asked whether the wettability of the substrate had any connection with the wettability of pigments, and secondly could air drying systems be made from water soluble alkyds.

MR. BRETT said that the pigment did not have much effect on wettability. To the second question he said that the maleinised oils would dry in 4-5 hours, but tended to be water sensitive. However, work was being carried out to develop glossy emulsions using water thinnable alkyds.

MR. HEASON asked if reactive pigments such as zinc oxide aided solubility of the resin and did this assist the cure.

MR. BRETT said that poor storage stability was observed due to the formation of zinc soaps which were thrown out of solution. In fact a certain amount of pigment selection had to be done to make sure of paint stability.

MR. HAIGH referred to the TMP/adipic acid/diol/methoxylated melamine system, and to the fact that there was a low rate of cure except in the presence of strong acid. Was there, he asked, any parallel with acid cured alkyd/melamine organic solvent systems.

MR. BRETT replied that in this connection reference was made to the effect of strong acid on the rate of cure in the context of the acid present as a reaction product of the resin components, and its release on stoving and resultant acceleration of cure ; not addition of, say, sulphonic acids, since the acid values of water soluble resins were already high.

The vote of thanks was given by Mr. D. R. Gray.

# O.C.C.A. TIE

The Council has authorised the production of an exclusive Tie for Members of the Oil & Colour Chemists' Association and it is expected that the ties will be available early in November. The Association's insignia will be woven in red and gold silk on a dark blue terylene background.

The tie will be sold only to Members of the Association for **20s.** (sterling) post free. If Members resident outside the continent of Europe wish the tie to be sent by airmail **5s.** (sterling) should be added to cover postage and insurance. The tie will be available only from :

**THRESHER & GLENNY**

**152/153 Strand, London, W.C.2**

and orders should be sent as soon as possible since it is expected that there will be a heavy initial demand.

*October, 1964*

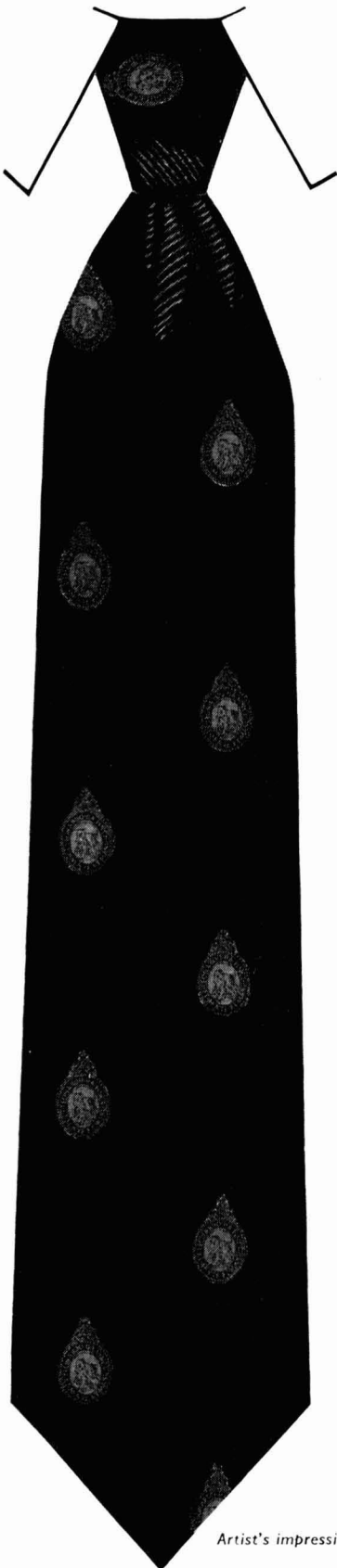
**To: Thresher and Glennly Ltd.,  
152/153 Strand, London, W.C.2.**

As a Member of the Association please accept, in advance, my order for an O.C.C.A. Tie. Remittance to the value of **20s.** (sterling) (if required to be sent by airmail to addresses outside Europe, please add **5s.** (sterling) to cover postage and insurance) is enclosed.

Name.....

Section.....

Address.....  
.....  
.....



*Artist's impression*

# Pure Compounds

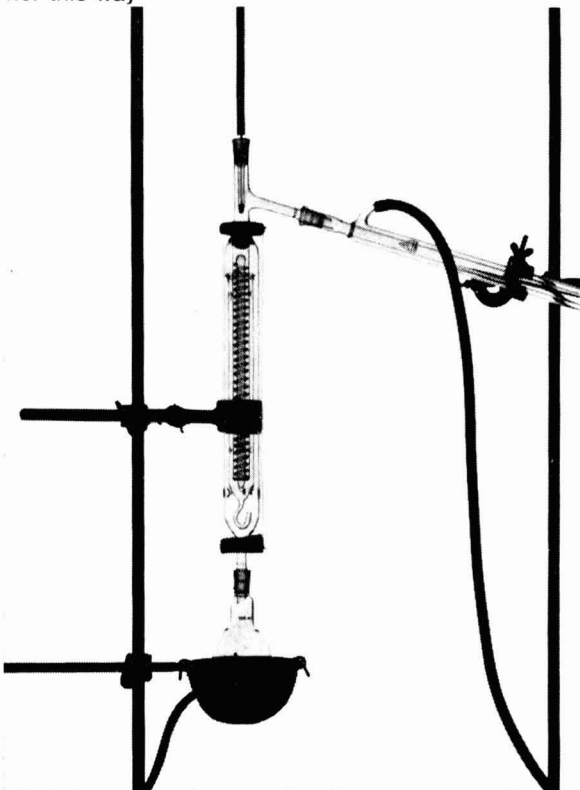


not this way



(Foto: Schweiz Pharmazie-Hist. Museum)

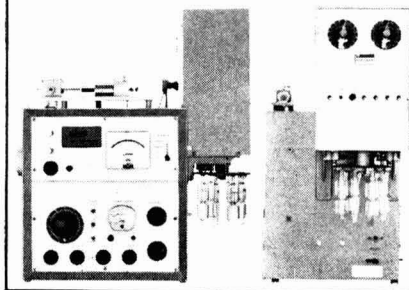
nor this way



But with a preparative  
Gas-Chromatograph—  
especially the reliable

## Autoprep

when preparing  
very pure compounds,  
this fully automatic,  
preparative Gas-Chromatograph  
will be your indispensable  
assistant



send for the Autoprep  
technical bulletin and  
your free subscription to  
Aerograph Research Notes.

## Wilkens

Wilkens Instrument + Research  
(U.K.) Ltd.  
Wythenshawe Civic Center  
Manchester, England

USA  
France  
Scandinavia  
Schweiz  
Germany  
Netherlands



# The Effects of Mineral Extenders on Anti-Corrosive Primers Based on Zinc Chromate

By P. DELFOSSE

OMYA. S.A., 30 Rue St. Augustine, Paris 2<sup>e</sup>, France

## Summary

*This investigation has shown the value of replacing part of zinc chromate by certain mineral extenders (substitution : 44.5 per cent by volume).*

*The differences in behaviour which are fairly substantial between the extenders examined have been determined. The kaolin paints, for example, give less good results ( $C_p=60.1$ ) than coatings containing pure zinc chromate ( $C_p=62.2$ ), while the coatings containing the surface treated calcite clearly give better protection ( $C_p=75.1$ ).*

## Rôle des Charges Minérales Diluants dans les Peintures Anti-Rouille à Base de Chromate de Zinc

### Résumé

*Cette étude a montré les avantages dus au remplacement d'une partie du Chromate de zinc par certaines charges minérales (substitution, 44, 5 per cent en volume).*

*Des différences de comportement assez importantes ont été observée parmi les charges soumises à l'examen. Les peintures au kaolin par exemple donnent des résultats inférieurs ( $C_p=60,1$ ) à ceux des revêtements contenant du Chromate de Zinc pur ( $C_p=62,2$ ) les Peintures contenant la calcite traitée en surface donnent sans aucune doute la meilleure protection ( $C_p=75,1$ ).*

## Einfluss von Mineral-Füllstoffen in Rostschutzfarben auf Basis Zinkchromat

### Zusammenfassung

*Bei dieser Untersuchung ergab es sich vorteilhaft einen Teil des Zinkchromats durch gewisse Mineral-Füllstoffe zu ersetzen (44,5% des Volumens).*

*Es wurden die Unterschiede der verwendeten Füllstoffe bei beschleunigten Älterungen geprüft. Diese Unterschiede können beträchtlich sein. Mit Rostschutzfarben die Kaolin enthalten, erzielt man weniger gute Ergebnisse ( $C_p=60,1$ ) als mit Farben mit reinen Zinkchromat ( $C_p=62,2$ ); Überzüge die oberflächen-behandelter Kalzit enthalten, ergeben jedoch einwandfrei einen besseren Schutz ( $C_p=75,1$ ).*

## INTRODUCTION

It may be useful to draw attention to the major progress that has been made in the last decade by the manufacturers of mineral extenders. This progress has been in three directions : achieving complete control of particle size distribution, ensuring perfect uniformity and reproducibility from batch to batch and providing surface treatments for the elementary particles.

Gradually the mineral extender has ceased to be regarded as an adulterant which always cost too much and whose sole purpose is to reduce the price to the customer. Many paint manufacturers today have come to appreciate the important part that can be played in paints by suitably chosen and sized mineral extenders.

With this in mind it is necessary to emphasise the great difference in behaviour that must be expected between what may be called 'extenders' of controlled particle size distribution on the one hand, and on the other hand the fillers with a very wide and irregular distribution of particle sizes, the latter acting as adulterants degrading the properties of the paint film.

Although mineral extenders have been used in anticorrosive paints for a considerable time, their use is nevertheless not as widespread as in decorative paints.

It is known that calcium carbonate of the chalk type may be used to advantage in anticorrosive paints with a drying oil base and that the excellent durability of these paints in very corrosive atmospheres may be attributed to the formation of calcium salts which give the dry film a special structure. In spite of this, calcium carbonate is rarely employed. This may be due to some extent to the harmful and unjustified ideas attached to the word 'chalk' but the major reason, without doubt, is the rigid and antiquated specifications which forbid the use of mineral extenders in paints intended for various authorities. It is unanimously agreed that these restrictions, which are very often unnecessarily excessive, arise solely from an ignorance of the behaviour of extenders, their possibilities and also their limitations.

The objects of the present work are therefore to try to outline the advantages and the disadvantages that may result from the use of mineral extenders in anticorrosive paints. It is particularly intended to deal with the problem in the light of the progress made in recent years in the extender field.

The mineral extenders were selected for study on several grounds,

(i) finding a type representative of each large chemical group, (ii) limiting their number to a minimum and (iii) selecting sufficiently developed extenders in each category for them to be called either 'extenders' or non-degrading 'adulterants' representing the optimum that may be achieved with the present state of grinding and selection techniques.

Since this study has the character of orientation and preselection work, artificial ageing tests were used in spite of the reservations and criticisms which may be put forward about them. It is undeniable that the quality of artificial ultra-violet light does not match the quality of sunlight. However, in order to limit errors of judgment resulting from observations made after artificial ageing as far as possible, each paint was subjected to four different systems of ageing.

The observations made from these tests taken as a whole thus offer a satisfactory guarantee of reproducibility and thus achieve the aims of this work.

#### EXPERIMENTAL

The paints were pigmented to give a Pigment Volume Concentration of 45 per cent. The binder used was a mixture of equal parts of a phenol-formaldehyde resin, wood oil and linseed oil according to the overall formulation :

phenol-formaldehyde resin	500 (acid value 15-25, type)
tung oil	500
linseed oil, 90 poise	500
white spirit	1100
butyl alcohol	100

The pigment volume concentration was maintained at 45 per cent.

To study the effect of the various extenders, 44.5 per cent of the inhibitive pigment by volume was replaced. The extenders used were as follows :

EXTENDERS	Code
chalk	1
asbestos powder	2
natural barium sulphate	3
washed kaolin	4
hydrophobic crystalline calcite (OMYA BLP.3)	5

### Preparation of the Paints

The binder was prepared in the following way. The resin and the tung oil were brought to 260°C for 15 minutes and then the linseed oil was added slowly while the temperature was maintained. After the addition of linseed oil the mixture was cooled and diluted.

The pigments and extenders were then incorporated together with the driers and the white spirit was used to adjust the viscosity to 160-180 secs, Ford cup No. 4 at 25°C. The paints were ground to obtain an average gauge reading of 6 to 7.

### Method of Applying the Paints

The paints were applied by brushing to steel panels 15 cm by 10 cm in size. The average dry film thickness was 70 microns.

The surface of the test piece to be painted was perfectly polished ; the other surface was provided with a coat of protective paint. Before the test panels were subjected to various ageing tests, all the paints were allowed to dry for seven days in the atmosphere. In order to avoid the initiation of corrosion from the rim of metal panels, the panel edges were immersed for a few millimetres in molten paraffin wax. Finally a diagonal scratch was cut through the dry film down to the metal.

### Ageing Tests

The test panels were subjected to various ageing methods to accelerate corrosion and simulate all the possible exposure conditions.

#### *Accelerated Ageing*

In the apparatus used the panels were subjected to continuous ultra-violet radiation accompanied by an intermittent salt spray (conditions of DEF 1053).

#### *Salt Spray*

The panels were exposed to an intermittent salt spray while remaining continuously in a moist salt-laden atmosphere. The cycle in this apparatus was eight hours' salt spray, then 16 hours' salt atmosphere.

#### *Moist Atmosphere*

The panels were placed in an oven where the atmosphere had a humidity of 100 per cent at a constant temperature of 42-48°C.

### *Aerated Sea Water*

In order to reproduce extreme marine conditions the panels were immersed in constantly aerated sea water in order to produce the severest corrosion conditions, *i.e.* the presence of oxygen and a liquid electrolyte.

### **Description and Characteristics of the Extenders Investigated**

Extenders were chosen for this investigation whose chemical composition and structure differed.

Two natural calcium carbonates :

- Amorphous—natural chalk (Code 1)  
Crystalline—surface treated calcite (Code 5)

Three non-carbonate extenders :

- An extender of fibrous structure—asbestine (Code 2)  
Natural crystalline barium sulphate (Code 3)  
An extender of lamellar structure—kaolin (Code 4)

These extenders were selected from amongst those of smallest particle size available commercially. Of these products the calcite is an extender whose surface has been modified by a physico-chemical reaction. This grade, intended for use in the paint industry, has been widely employed in architectural paints. Its completely hydrophobic nature is a factor which would appear to be of particular interest for study.

PHYSICAL CHARACTERISTICS OF THE PIGMENTS STUDIED

<i>Fineness</i>	<i>Chalk</i>	<i>Asbestine</i>	<i>BaSO<sub>4</sub></i>	<i>Kaolin</i>	<i>Calcite</i>
Residue T200 (74 $\mu$ mesh)	0.5	1.1	0.03	0.02	none
Residue T325 (43 $\mu$ mesh)	1.6	6.7	0.1	0.2	0.01
Particle size distribution	1-40 $\mu$	2.5-100 $\mu$	2-40 $\mu$	0.7-40 $\mu$	1.5-20 $\mu$
Mean statistical diameter (equivalent)	2.5 $\mu$	8 $\mu$ *	10 $\mu$	2.5 $\mu$	4.5 $\mu$
<i>Dry Whiteness : MgO=100</i>					
Green tristimulus filter	85	89	93	90.5	90.5
Yellow	86.5	89.5	95	90	92
Blue	79	87	91	86.5	86
White Index $I = \frac{Y-B}{G} \times 100$	+9	+3	+4	+4	+7
<i>Whiteness in Oil :</i>					
Blue filter (based on MgO)	31	34.5	51	28.5	53.5
S.G.	2.7	3.2	4.3	2.6	2.7
Particle shape	Spherical	Fibrous	Crystalline	Lamellar	Rhombohedral
<i>Oil Absorption :</i>					
(a) rub out test g. oil/100g powder	16	29.76	9.3	41.4	15
(b) Gardner Coleman cc oil / g. powder	24.75	42.5	14.5	63	17.5
CPVC percentage	68.5	49.5	70	46.5	69.7

\*The mean particle size for asbestine corresponds to the mean of the dimensions of particles measured parallel to the orientation of these particles.

### Interpretation of the Results

The observations made on the panels after ageing were divided into two groups :

Examination of the film.

Examination of the metal beneath (after removing the paint film with solvent).

#### *Examination of the Film*

The following phenomena were examined in turn :

##### *Appearance of rust through the film.*

Particular attention is given as to whether the rust has appeared along the scratch or all over the surface.

##### *Blistering.*

Number and distribution of blisters.

##### *Adhesion of the film to the metal.*

#### *Examination of the Underlying Metal*

*Oxidation of the metal* over the whole surface.

*State of the metal* along the diagonal scratch.

Each of the phenomena observed was given a rating of  $\alpha$  of from 1 to 6 according to the following definitions :

6 excellent	3 poor
5 very good	2 bad
4 good	1 very bad

On the other hand the observed phenomena do not have the same practical importance and the ratings were therefore modified by a coefficient  $a$  which was selected according to the importance of the factor :

	$a$
Metal oxidation .. .. .	4
Corrosion along the scratch .. .. .	3.5
Rusting through the film .. .. .	3
Film adherence .. .. .	3
Blistering (examination of the film at $\times 20$ magnification shows no major cracking) .. .. .	2

These coefficients are, no doubt, open to criticism since certain of the phenomena are more or less interdependent. Just because of this relationship the differences between these coefficients have been held as small as possible while taking into account, through the value of the coefficient, the practical effect of a change in the film or the support.

In each series for each extender and each type of ageing a calculation has been made for the sum of the products

$$a_{i_1} \alpha_{i_1} + a_{i_2} \alpha_{i_2} + \dots + a_{i_5} \alpha_{i_5}$$

$i$  being the observed phenomena (of which there are five here).

For each type of ageing  $v$  a sum is therefore obtained of

$$Sv = \sum_{i_1}^{i_5} a_i \alpha_i$$

By adding the values of  $S$  for a given pigment in the four types of ageing a sum is obtained of

$$C_p = \frac{1}{v} \sum_{v_1}^{v_4} S_{v_i}$$

$C_p$  is the gradient used as the final classification, *i.e.*

$$C_p = \frac{1}{v} \sum_{v_1}^{v_4} \sum_{i_1}^{i_5} a_i \alpha_i$$

B Paint based on a compound binder  
g Pigment : Zinc chromate

	S.G.	Unfilled paint		Paint with extender					
		vol.	wt $Bg_0$	vol	wt $Bg_1$	wt $Bg_2$	wt $Bg_3$	wt $Bg_4$	wt $Bg_5$
Zinc chromate	3.2	81	259	45	144	144	144	144	144
Titanium dioxide	4.26	9	37.8	9	37.8	37.8	37.8	37.8	37.8
Binder*	1	110	200	110	200	200	200	200	200
White spirit	—	—	154	—	96	96	82	108	96
Lead naphthenate 24 per cent	—	—	2.34	—	2.34	2.34	2.34	2.34	2.34
Cobalt naphthenate 6 per cent	—	—	1.86	—	1.86	1.86	1.86	1.86	1.86
Chalk	2.7	—	—	36	97	—	—	—	—
Asbestos	3.25	—	—	36	—	113.4	—	—	—
Barium sulphate	4.4	—	—	36	—	—	145	—	—
Kaolin	2.65	—	—	36	—	—	—	93.6	—
Calcite	2.7	—	—	36	—	—	—	—	97
Pigment volume concentration			45%		45%	45%	45%	45%	45%

\*Binder formulation : *Beckacite* 1123 500  
 Tung oil 500  
 Linseed oil, 90 poise 500  
 White spirit 1100  
 Butyl alcohol 100

Volumetric substitution of  $\frac{81-45}{90} \times 100$  of the total volume of the pigments equals 40 per cent which represents  $\frac{259-144}{259} \times 100 = 44.5$  per cent of the inhibitive pigment.

## OBSERVATIONS AFTER AGEING

### Accelerated Ageing, 500 hours.

#### Examination of the Film

*Blistering.* There was no blistering in the case of the standard. Very slight blistering occurred with asbestine and more serious blistering in the case of kaolin and barium sulphate.

#### Ratings

<i>Standard</i>	<i>Asbestine</i>	<i>Chalk</i>	<i>Calcite</i>	<i>Kaolin</i>	<i>Barium Sulphate</i>
6	5	3.5	3	2.5	2

*Appearance of rusting through the film.* There was no rusting through the film except in the case of barium sulphate, where there were a few isolated spots.

*Ratings*

Standard	Chalk	Kaolin	Calcite	Asbestine	Barium Sulphate
6	6	6	6	5.5	5

*Adherence.* The zinc chromate paints had excellent adherence except the paint containing kaolin.

*Ratings*

Chalk	Asbestine	Barium Sulphate	Calcite	Standard	Kaolin
6	6	6	5	5	3

*Examination of the Support*

*Metal corrosion.* No corrosion appeared over the whole plate except in the case of kaolin where there were fine pits.

*Ratings*

Standard	Chalk	Asbestine	Barium Sulphate	Calcite	Kaolin
5	4.5	4.5	4.5	4.5	3.5

*Corrosion along the scratch.* There was none except in the case of asbestine.

*Ratings*

Standard	Barium Sulphate	Kaolin	Calcite	Chalk	Asbestine
6	6	6	6	5.5	4

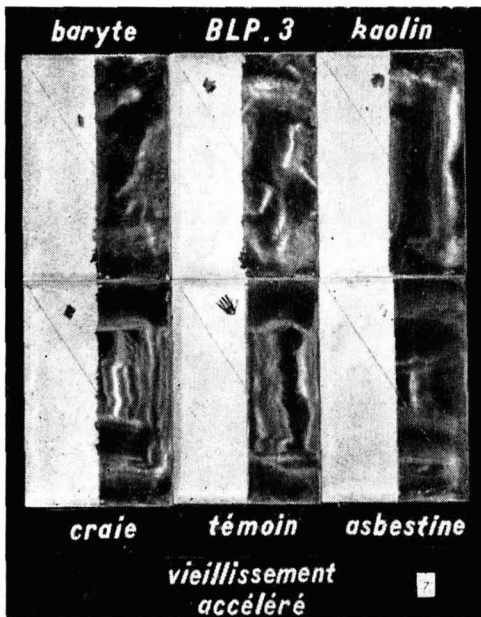


FIG. 1. PANELS AFTER ACCELERATED WEATHERING

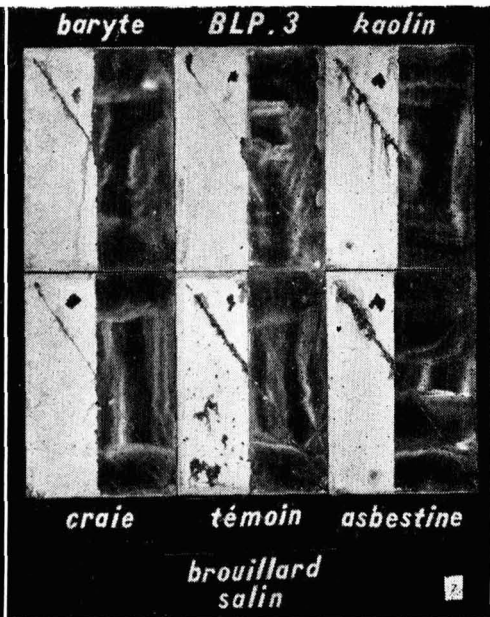


FIG. 2. PANELS AFTER EXPOSURE TO SALT SPRAY



**Salt Spray Ageing, 768 hours.***Examination of the Film*

*Blistering.* In the case of the paint without extender there was marked and very widespread blistering. In the case of asbestine, blistering appeared along the scratch. Blistering was negligible in the case of barium sulphate and kaolin and there did not appear to be blistering in the case of calcite.

*Ratings*

<i>Calcite</i>	<i>Barium Sulphate</i>	<i>Kaolin</i>	<i>Chalk</i>	<i>Asbestine</i>	<i>Standard</i>
6	5	5	5	3	2.5

*Appearance of rusting through the film.* Very slight rusting appeared with the paint not containing extender near to the blisters and along the scratch. It also appeared to a major degree along the scratch with the paints containing asbestine and kaolin, the best performance being given here by chalk and the surface treated calcide.

*Ratings*

<i>Chalk</i>	<i>Calcite</i>	<i>Barium Sulphate</i>	<i>Kaolin</i>	<i>Asbestine</i>	<i>Standard</i>
5	5	4.5	3	2	1.5

*Adhesion.* In this series the paint containing the surface treated calcite gave improved adhesion over the standard paint, which in itself was very good. The other extenders (chalk, asbestine, barium sulphate and kaolin) substantially decreased the adhesion, as shown by the ratings below.

*Ratings*

<i>Calcite</i>	<i>Standard</i>	<i>Chalk</i>	<i>Barium Sulphate</i>	<i>Asbestine</i>	<i>Kaolin</i>
6	5	4.5	3	2	2

**Examination of the Support**

*Metal corrosion.* The metal corrosion was very serious in the case of the unextended paint, particularly along the scratch and in a few isolated points where it was relatively extensive at points where the paint had blistered. Corrosion was virtually insignificant in the other cases, being slightly more serious with small dispersed pits in the case of barium sulphate and kaolin.

*Ratings*

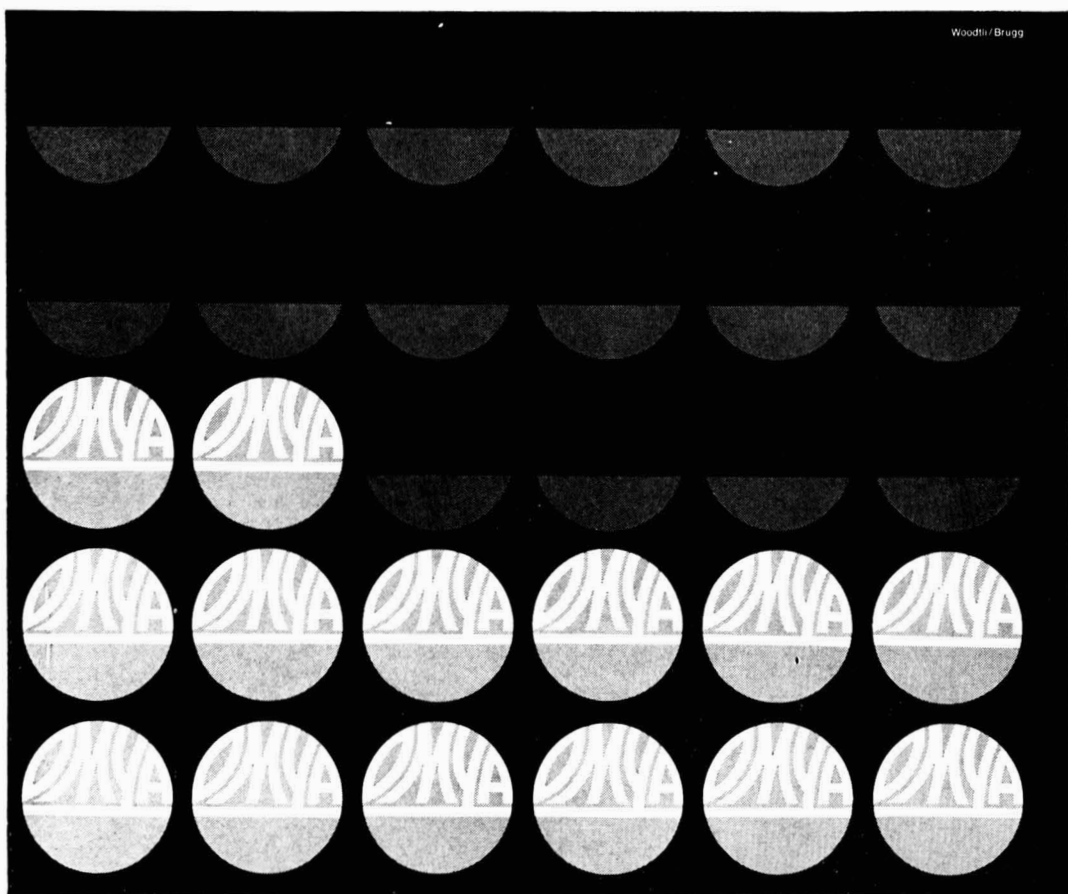
<i>Calcite</i>	<i>Chalk</i>	<i>Asbestine</i>	<i>Barium Sulphate</i>	<i>Kaolin</i>	<i>Standard</i>
5	5	5	4	4	2

*Corrosion along the scratch.* Corrosion along the scratch was very pronounced and relatively deep in the case of the standard panel. It was practically negligible for the other paints.

*Ratings*

<i>Chalk</i>	<i>Asbestine</i>	<i>Barium Sulphate</i>	<i>Kaolin</i>	<i>Calcite</i>	<i>Standard</i>
4.5	4.5	4.5	4.5	4.5	2

## Fillers and Extenders for the Paint Industry



Sole British Representatives:  
Croxtan & Garry Limited  
27, St. James's Road, Kingston-upon-Thames, Surrey  
Telephone: KINGston 9444 (P.B.X.)

***Please Help***

**THE PAINT TRADE**

**BENEVOLENT FUND**

The Fund was established in 1935 to provide assistance by grants or loans to necessitous cases amongst persons engaged in the colour, paint and varnish industries and to the widows and other dependants of persons lately engaged in those industries.

Pension schemes and the "Welfare State" are unfortunately not always adequate to meet difficult circumstances at a given time. It is in such cases that the Fund can be of practical assistance.

Finance is obtained by voluntary gifts from firms and individuals by way of covenanted subscriptions, annual subscriptions and donations, supplemented mainly by money raised by an annual golf competition. The Fund costs very little to administer as all services are given voluntarily.

For many years the income from these sources proved adequate to meet the yearly grants paid. This is no longer so.

Contributions are therefore greatly needed and should be sent to :

HONORARY SECRETARY, PAINT TRADE BENEVOLENT FUND,  
PRUDENTIAL HOUSE, WELLESLEY ROAD, CROYDON, SURREY

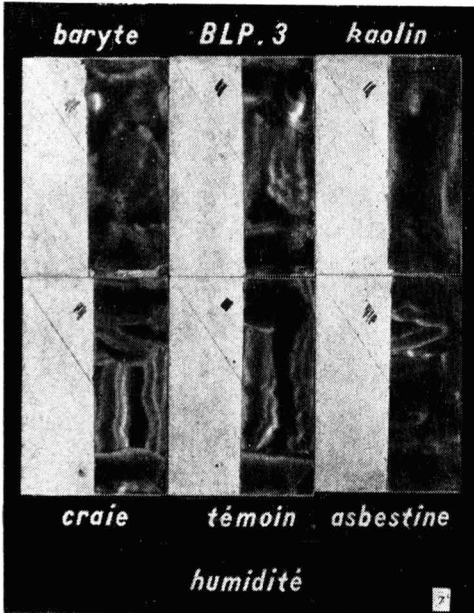


FIG. 3. PANELS AFTER EXPOSURE TO 100 PER CENT HUMIDITY

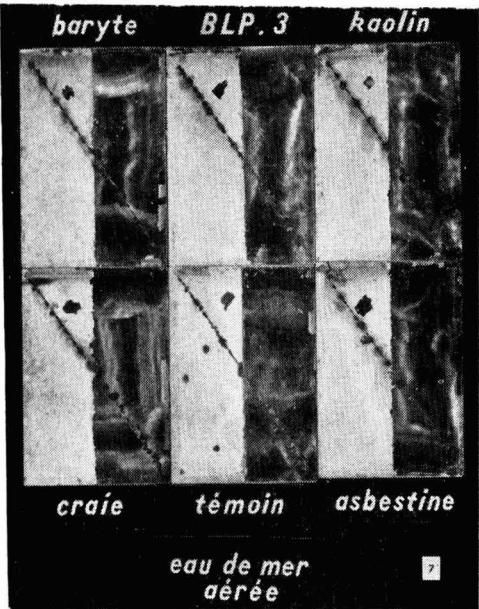


FIG. 4. PANELS AFTER IMMERSION IN AERATED SEA WATER

**Ageing in 100 per cent Humidity, 42-48°C, 936 hours.**

*Examination of the Film*

*Blistering.* Blistering was virtually absent in the case of the unextended sample. It appeared along the scratch and at the panel edges in the case of asbestine, barium sulphate and the surface treated calcite. It was a little less serious in the case of kaolin and chalk.

*Ratings*

Standard	Chalk	Kaolin	Calcite	Barium Sulphate	Asbestine
5	3.5	3	3	2.5	2.5

*Appearance of rust through the film.* There was practically no rusting through of the film.

*Ratings*

Standard	Chalk	Asbestine	Barium Sulphate	Kaolin	Calcite
5	5	5	5	5	5

*Adhesion.* The adhesion of the film was generally very good and was excellent in the case of chalk and the surface treated calcite.

*Ratings*

Chalk	Calcite	Asbestine	Kaolin	Standard	Barium Sulphate
6	6	5	5	5	4

*Examination of the Support*

*Metal corrosion.* There was no corrosion of the metal in the case of the surface treated calcite. It was slight at a few points in the case of standard and the most in the case of kaolin.

*Ratings*

<i>Calcite</i>	<i>Standard</i>	<i>Chalk</i>	<i>Asbestine</i>	<i>Barium Sulphate</i>	<i>Kaolin</i>
6	5	4.5	4.5	4	3

*Corrosion along the scratch.* Corrosion along the scratch was absent with calcite and the standard. It was more serious for chalk, barium sulphate and asbestine.

<i>Standard</i>	<i>Calcite</i>	<i>Kaolin</i>	<i>Chalk</i>	<i>Barium Sulphate</i>	<i>Asbestine</i>
6	6	5	4	4	4

*Ageing in Aerated Sea Water, 1,056 hours.**Examination of the Film*

*Blistering.* The only blistering that occurred was in the form of very large blisters alongside the scratch. In the case of the standard there was some major blistering over the remainder of the film.

*Ratings*

<i>Chalk</i>	<i>Asbestine</i>	<i>Barium Sulphate</i>	<i>Kaolin</i>	<i>Calcite</i>	<i>Standard</i>
4	4	4	4	4	3

*Appearance of rust through the film.* Rusting through the film occurred adjacent to the blisters. It occurred in the form of fairly large spots along the scratch line, particularly in the case of asbestine.

*Ratings*

<i>Chalk</i>	<i>Barium Sulphate</i>	<i>Kaolin</i>	<i>Calcite</i>	<i>Asbestine</i>	<i>Standard</i>
3.5	3	3	3	2	2

*Adhesion.* Of the extenders examined, only barium sulphate and the surface treated calcite enabled the film adhesion to be maintained at the same level as in the standard.

*Ratings*

<i>Standard</i>	<i>Barium Sulphate</i>	<i>Calcite</i>	<i>Kaolin</i>	<i>Asbestine</i>	<i>Chalk</i>
4.5	4.5	4	3.5	3	2.5

*Examination of the Support*

*Metal corrosion.* In the case of the standard, the metal panel showed three or four local rust attacks. In the case of kaolin there was slight oxidation over about 25 per cent of the surface. No corrosion of the metal was noted in the case of chalk, asbestine, barium sulphate and the surface treated calcite.

*Ratings*

<i>Chalk</i>	<i>Asbestine</i>	<i>Barium Sulphate</i>	<i>Calcite</i>	<i>Kaolin</i>	<i>Standard</i>
5	5	5	5	3	2.5

*Corrosion along the scratch.* Corrosion along the scratch was linked with blistering. It was present in the form of fairly large spots distributed along the scratch.

### Ratings

<i>Barium Sulphate</i>	<i>Chalk</i>	<i>Asbestine</i>	<i>Kaolin</i>	<i>Calcite</i>	<i>Standard</i>
3	2.5	2.5	2.5	2.5	2

B. PAINT BASED ON A COMPOUND BINDER

g PIGMENT: ZINC CHROMATE

coefficient $a$	<i>Standard</i> $Bg_0$	<i>Chalk</i> $Bg_1$	<i>Asbestine</i> $Bg_2$	<i>Barium Sulphate</i> $Bg_3$	<i>Kaolin</i> $Bg_4$	<i>Calcite</i> $Bg_5$
		$a \times$	rating $\alpha$			
<i>Accelerated ageing, 500 hours</i>						
blistering $\times 2$	12	7	10	4	5	6
metal oxidation $\times 4$	20	18	18	18	14	18
rusting through the film $\times 3$	18	18	16.5	15	18	18
corrosion along the scratch $\times 3.5$	21	19.25	14	21	21	21
film adherence $\times 3$	15	18	18	18	9	15
Total $S_v = \sum_{i=1}^{i_5} a_i \alpha_i$	86	80.25	76.5	76	67	78
<i>Salt Spray Ageing, 768 hours</i>						
blistering $\times 2$	5	10	6	10	10	12
metal oxidation $\times 4$	8	20	20	16	16	20
rusting through the film $\times 3$	4.5	15	6	13.5	9	15
corrosion along the scratch $\times 3.5$	7	15.75	15.75	15.75	15.75	15.75
film adherence $\times 3$	15	13.5	6	9	6	18
Total $S_v = \sum_{i=1}^{i_5} a_i \alpha_i$	39.5	74.25	53.75	64.25	56.75	80.75
<i>Ageing in 100 per cent humidity, 42-48°C, 936 hours</i>						
blistering $\times 2$	10	7	5	5	6	6
metal oxidation $\times 4$	20	18	18	16	12	24
rusting through the film $\times 3$	15	15	15	15	15	15
corrosion along the scratch $\times 3.5$	21	14	14	14	17.5	21
film adherence $\times 3$	15	18	15	12	15	18
Total $S_v = \sum_{i=1}^{i_5} a_i \alpha_i$	81	72	67	62	65.5	84
<i>Ageing in Aerated Sea Water, 1056 hours</i>						
blistering $\times 2$	6	8	8	8	8	8
metal oxidation $\times 4$	10	20	20	20	12	20
rusting through the film $\times 3$	6	10.5	6	9	9	9
corrosion along the scratch $\times 3.5$	7	8.75	8.75	10.5	8.75	8.75
film adherence $\times 3$	13.5	7.5	9	13.5	13.5	12
Total $S_v = \sum_{i=1}^{i_5} a_i \alpha_i$	42.5	54.75	51.75	61	51.25	57.75
T : general total $\sum_{v=1}^{v_4} S_v$	249	281.25	249	263.25	240.5	300.5
$C_p = \frac{1}{v} \sum_{v=1}^{v_4} S_v$	62.2	70.3	62.2	65.8	60.1	75.1



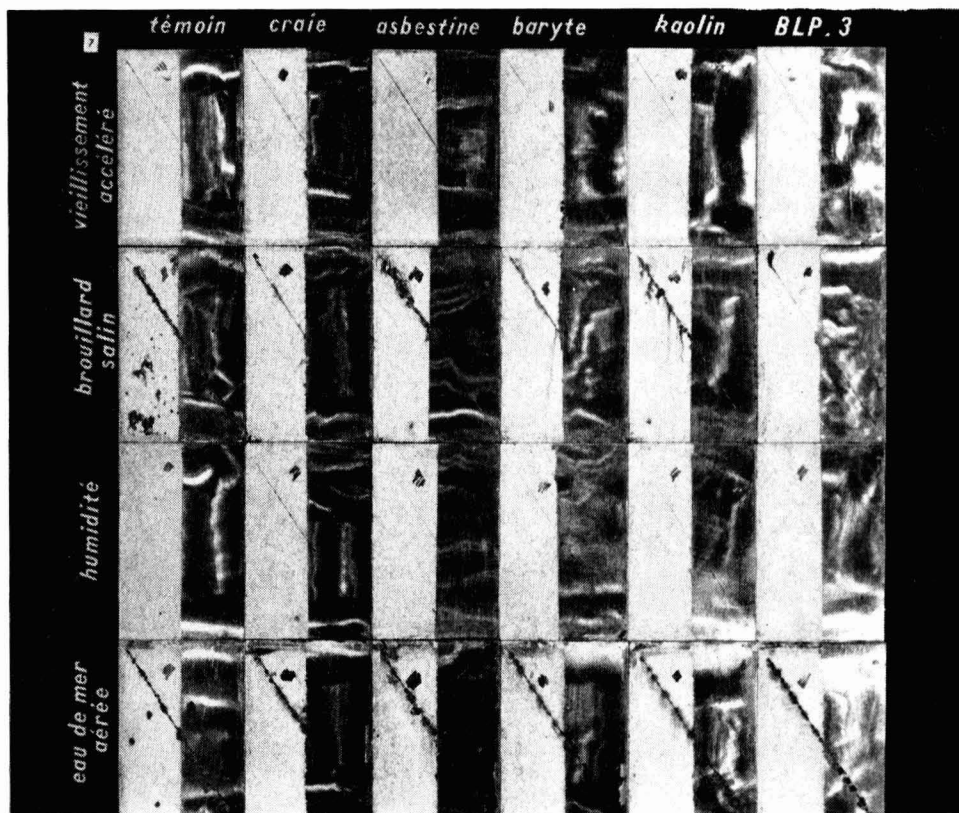


FIG. 5. PANELS OF A PAINT BASED ON A COMPOUND BINDER AFTER EXPOSURE TO VARIOUS TEST CONDITIONS

### CONCLUSION

In the case of accelerated ageing and ageing in a moist hot atmosphere, most of the extenders favour blistering. On the other hand in a moist salt atmosphere, blistering is clearly greater with the unextended paints, and certain extenders, reduce the blistering or even eliminate it, as with the surface treated calcite.

The oxidation of the metal and the appearance of rusting through the film are very marked in the case of the standard, while the coatings containing the surface treated calcite, on the other hand, give better performance. A clear improvement in adherence is also noted with this latter extender.

Kaolin in the salt spray test and accelerated ageing gives films of very poor adhesion.

The surface treated calcite is clearly to be found on the highest level ( $C=75.1$ ) followed by chalk with  $C=70.3$ . Kaolin, on the other hand, gives less good results with a level of  $C=60.1$

It is possible to take into account the effect of each extender on the various observed phenomena by adding the products  $a_i \alpha_i$  obtained by the four types of

ageing corresponding to a predetermined degradation (i). It is also possible to link the behaviour of a given extender with the phenomenon of blistering or metal oxidation or any other change. In this case the sum may be expressed as

$$S_i = \sum_{v_1}^{v_4} a_i \alpha_i$$

The following table indicates the values of  $S_{i_1}$  to  $S_{i_5}$  for the five phenomena:

$$S_i = \sum_{v_1}^{v_4} a_i \alpha_i$$

Phenomenon observed		<i>Standard</i>	<i>Chalk</i>	<i>Asbestine</i>	<i>Barium Sulphate</i>	<i>Kaolin</i>	<i>Calcite</i>
Blistering	$S_{i_1}$	33	32	29	27	29	32
Metal oxidation	$S_{i_2}$	58	76	76	70	54	82
Rusting through the film	$S_{i_3}$	43.5	58.5	43.5	52.5	51	57
Corrosion along the scratch	$S_{i_4}$	56	57.75	52.50	61.25	63	66.50
Film adherence	$S_{i_5}$	58.5	57	48	52.5	43.5	63
		249.0	281.25	249.0	263.25	240.5	300.50

It has been shown that the mineral extenders have little influence on blistering ; on the other hand, metal oxidation beneath the film is greatly reduced by all the extenders except kaolin ( $S_{i_2}=54$ ). From this point of view the surface treated calcite gives better results with a level of  $S_{i_2}=82$  against 58 for the unextended paint. The appearance of rust through the film is also reduced in relation to a standard coating ( $S_{i_3}=43.5$ ) especially in the case of formulations containing the surface treated calcite  $S_{i_3}=57$  and chalk  $S_{i_3}=58.5$ .

The surface treated calcite is also superior as regards corrosion along the scratch :  $S_{i_4}=66.5$  against  $S_{i_4}=56$  for the standard paint. Finally it has been shown that amongst the five extenders examined, the surface treated calcite improves film adherence ( $S_{i_5}=63$ ) compared with the standard ( $S_{i_5}=58.5$ ).

[Received 12 March 1964

# A Method for the Measurement of the Adhesion of Surface Coatings Under Service Conditions

By M. W. HOLLOWAY and P. A. WALKER

Atomic Energy Authority (AWRE), Building SB43, Aldermaston, Berks

## Summary

*A simple, inexpensive method for the measurement of the adhesion of surface coatings has been developed. Use is made of a recording torque spanner to apply a shear force to the paint system (via a metal cylinder bonded to the coated surface). The method is applicable to painted components in service, since, although causing local damage to the coating system, the component is undamaged. The method provides a useful tool in the investigation of the effectiveness of surface pretreatment, presence of etch primer, degree of cure, and suspected poor adhesion in service.*

## Une Méthode Permettant le Mesurage—en cours de Service—de l'adhésion des Couches de Surface

### Résumé

*Une méthode simple, peu coûteuse, a été mise au point pour mesurer l'adhésion des couches de surface. Une clé dynamométrique enregistreuse est utilisée afin d'appliquer une résistance au cisaillement à la couche de peinture (grâce à un cylindre métallique appliqué sur la surface enduite). La méthode est applicable aux pièces composantes peintes et ceci en cours de service, car, bien que la couche de peinture subisse par endroits une détérioration, la pièce composante reste intacte. Cette méthode s'avère très utile lors des recherches touchant à l'efficacité du traitement préalable de surface, à la présence de corrosion affectant la couche d'impression, au degré de cuisson et à une adhésion faible, suspectée en cours de service.*

## Eine Methode zur Messung der Oberflächen-Adhäsion von Lack-Überzügen

### Zusammenfassung

*Es handelt sich um eine einfache und billige Methode, zur Messung der Oberflächen-Adhäsion von Lack-Überzügen. Es wird dabei ein kalibrierter Drehmomentschlüssel verwendet, um auf den Überzug eine Schubkraft einwirken zu lassen (über einen Metallzylinder, der mit der Oberfläche verbunden ist). Diese Messmethode lässt sich auch bei Teilen anwenden, die ständig in Betrieb sind; denn der Überzug wird zwar angegriffen, das Teil bleibt jedoch unversehrt. Die Methode ist nützlich, wenn es darum geht, festzustellen, ob die Vorbehandlung der Oberfläche gut war, ob ein Grundiermittel vorhanden ist, wie schnell die Austrocknung vonstatten geht und wie sich der Überzug bei Beanspruchung verhält.*

## INTRODUCTION

A fundamental requirement of surface coatings is that they adhere to the surface which has been coated, since to decorate or protect the coating must remain in position. There is no evidence of a threshold value for adhesion below which the coating is non-adherent and above which satisfactory performance can be guaranteed. It is perhaps sufficient that the adhesion of the coating is great enough to withstand both the forces exterior to the paint film imposed upon it by the service environment, and the forces within the film caused by dimensional changes due to cure or progressive composition changes caused

by such hostile agencies as ultra-violet irradiation, oxygen attack. In practice many factors affect the adhesion of a coating, for example, composition of the vehicle, level of pigmentation, surface preparation and atmospheric humidity.

The problem of measuring the adhesion of surface coatings is difficult, even under laboratory conditions, and most if not all existing methods require the destruction of the component to be tested or the preparation of special test specimens coated under precise conditions. When some measure of adhesion under service conditions is required, the problem becomes more acute, since it is impossible to duplicate the precise situation, either from the viewpoint of application or the environment. Furthermore, it may be impossible to resort to methods involving the destruction of the component as this may be undesirable, costly or result in specimens which are unsuitable for the test method.

It is possible to assess the adhesion of coatings in service by means of a peel test involving the use of a suitable adhesive tape and this is commonly used where the adhesion is suspect. Unfortunately, the test is a subjective one and no indication of the value at which the adhesion has failed can be obtained. The method described in this paper does much to overcome the limitations of present methods.

#### METHODS OF MEASURING ADHESION

Existing methods of test may be separated into three distinct types depending on the principle involved ; these may be summarised as :

- (a) Inertia tests, which involve rapid acceleration or deceleration of the film with consequent detachment from the substrate.
- (b) Peel tests, in which some object is forced between the film and the substrate or the coating is stripped off by means of an adhesive tape.
- (c) Direct tensile tests, where a force is applied at right angles to the film by means of some object bonded to the surface.

Techniques utilising the first principle include the use of the high-speed centrifuge, the coated rotor being revolved at increasing speed until the film is detached. In practice, due to metal fatigue, the size of the rotor is limited, and in order to prevent heating effects due to friction, it is necessary to work under vacuum. The method is therefore only applicable to research investigation rather than service problems.

A similar method using the rapid deceleration of a high velocity projectile against a hard metal object has been proposed, the coated specimens being used as the projectiles. In this case the specimens are stamped from the painted object, which meets one objection raised, in that the conditions of application are precise, although since the method is destructive of the component, it is of limited applicability and cannot be used as a routine test.

Test methods involving the "peel" technique have received a great deal of attention and are currently used in many routine test procedures. In general the results obtained are of a subjective nature only and precise values cannot be obtained. A major problem in the interpretation of the results is that the

peeling process is influenced by other mechanical properties of the coating and the substrate.

Direct tensile tests in which a force is applied at right angles to the film by means of an object bonded to the surface have now come into prominence as high strength adhesives have been developed. One such method in which specially prepared metallic specimens are painted and bonded together and the resulting doublet broken on a tensometer has given extremely reproducible results. A logical development of this technique was to stamp out discs from the actual component and sandwich these between cylindrical test pieces. Although this overcame the problem of application variables, it still involved destruction of the component. This modified test may be described as the Sandwich Method<sup>1</sup>.

The Torque Method developed at AWRE to overcome these major drawbacks was an application of this shear technique, in which steel specimens were bonded to the surface of the component and removed by means of a recording torque spanner, the force applied being a shearing force only.

### DEVELOPMENT OF THE TORQUE METHOD

The use of a recording torque spanner for shear testing is not new ; a reference has been made to its use for determining the cure of concrete<sup>2</sup>, but in order to develop a method capable of giving reproducible results with surface coatings, considerable refinement was necessary.

#### Apparatus

##### *Selection of Torque Spanner*

It was estimated that the maximum shear stress likely to be necessary would be in the region of 4,800 lbf/in<sup>2</sup>, and it was thought that the maximum torque which could be applied comfortably to any specimen would be approximately 120 lb. A greater torque would lead to operator difficulties, particularly when carrying out tests on a vertical surface. The torque spanner selected was a Type A120 S-120 lb  $\frac{1}{4}$  in square drive, manufactured by the *MHH Engineering Company*, of Bramley, Guildford. Further torque spanners covering the range 5-700 lb in are available.

##### *Design of Test Specimens*

A cylindrical rod is stated to be subject to pure torsion, when this torsion is caused by a couple applied in such a manner that the axis of the couple coincides with the axis of the rod. The state of stress at any point in the cross-section of the rod is then one of pure shear according to the equation

$$\frac{T}{I_p} = \frac{f_s}{r} \dots\dots\dots (1)$$

where  $T$  = Torque in lbf/in

$I_p$  = Polar moment of Inertia of Section in inches<sup>4</sup>

$f_s$  = Shear stress at Radius  $r$  inches in lbf/in<sup>2</sup>

$$\text{from (1) } f_s = \frac{T \cdot r}{I_p} \dots\dots\dots (2)$$

It can be seen that for a given section having polar moment of inertia  $I_p$  with a constant torque  $T$  applied, the maximum shear stress will occur at the outer circumference of the section

$$I_p \text{ for a hollow cylinder} = \frac{\pi}{32} (D_o^4 - D_i^4) \dots\dots\dots (3)$$

where  $D_o$  = outer diameter of cylinder  
 $D_i$  = inner diameter of cylinder

Substituting (3) in (2) above and letting  $r = \frac{D_o}{2}$  we have

$$F_s \text{ (maximum)} = \frac{16 T D_o}{\pi(D_o^4 - D_i^4)} \dots\dots\dots (4)$$

hence  $T = f_s \text{ (maximum)} \frac{\pi}{16} \frac{D_o^4 - D_i^4}{D_o} \dots\dots\dots (5)$

Substituting the estimated values of 120 lb in for torque and 4,800 lbf/in<sup>2</sup> for the maximum shear stress in (5)

$$D_i^4 = D_o^4 - \frac{0.4}{\pi} D_o \dots\dots\dots (6)$$

From (6) it was possible to calculate a series of co-related diameters such that a range of test specimens of varying diameter could be manufactured. These are shown in Table I.

It was appreciated that these calculations would only apply precisely to ideal systems and might not be directly applicable to the substrate/paint/specimen system under test, due to factors not taken into account in the

TABLE I  
 CALCULATED CO-RELATED DIAMETERS

$D_o$	$D_o^4$	$\frac{0.4}{\pi} D_o$	$D_i^4$	$D_i$	Type
1.100	1.462	0.1401	1.3220	1.072	—
1.000	1.000	0.1275	0.8725	0.966	A
0.900	0.656	0.1147	0.5410	0.855	—
0.800	0.410	0.1019	0.3050	0.745	—
0.750	0.316	0.0955	0.2200	0.685	B
0.700	0.240	0.0891	0.1510	0.623	—
0.600	0.1298	0.0764	0.0534	0.486	—
0.520	0.0731	0.0662	0.0069	0.288	C
0.503	0.0640	0.0636	0	0	D

basic equations. In spite of this they provided a convenient starting point for the design of suitable test cylinders for practical evaluation.

Specimens were manufactured from stainless steel and the dimensions selected to cover a wide range of diameters, a dimensional tolerance of  $\pm 0.001$  in being applied to all specimens. A sketch of the general design is included as an appendix to this report and Fig. 1 shows typical specimens.

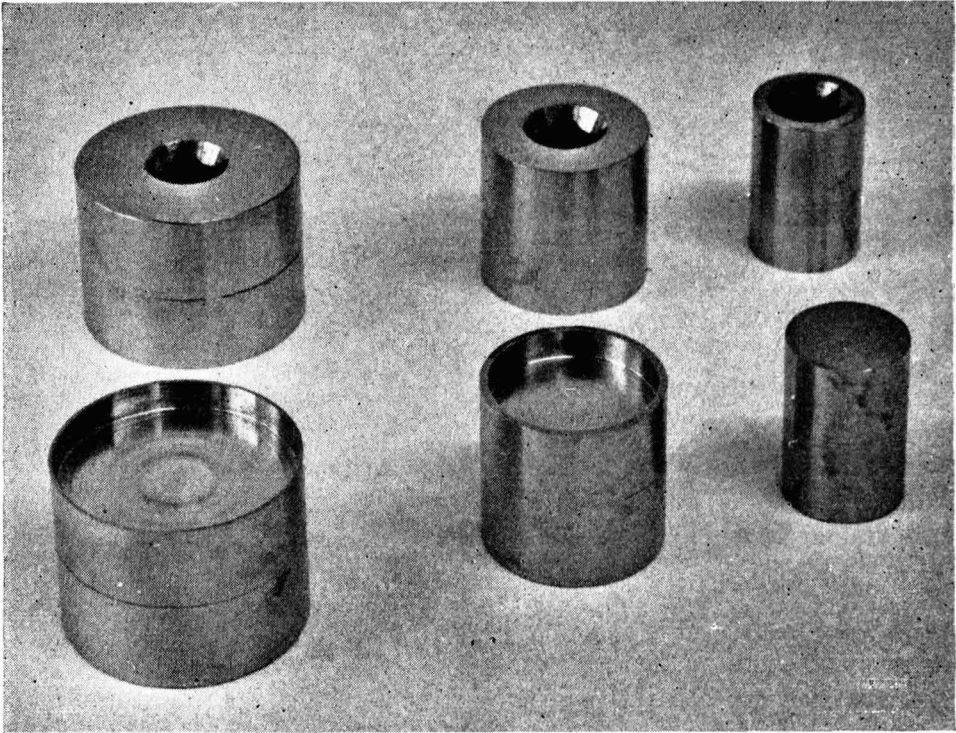


FIG. 1. TORQUE TEST SPECIMENS

#### *Coupling of Torque Spanner to Specimen*

Initial experiments showed that although every effort was made to apply only a shear force, some peel component was invariably introduced, and although the use of a universal joint materially reduced this component, the method was still subject to operator error. This was particularly so when tests were conducted on non-supported thin flexible substrates or on vertical surfaces. To overcome this difficulty a supporting table was designed such that the tendency of the substrate to flex was reduced to a minimum and the likelihood of a peel component substantially eliminated. A sketch of this supporting table is shown as an appendix to this report. Fig. 2 shows the ball race and connection with the adhesion specimen.



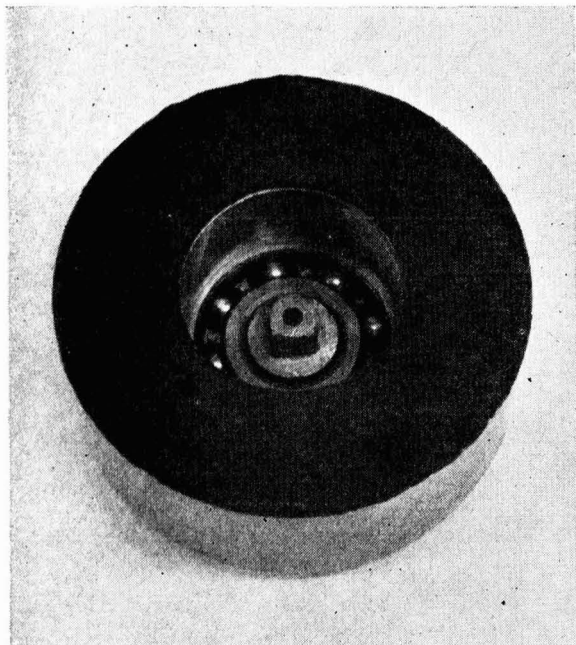


FIG. 2. SUPPORTING TABLE

## EXPERIMENTAL

The adhesive used is of particular importance in the determination of adhesion by this method and ideally should have the following properties: (a) high cohesive strength, (b) high adhesion to metal and paint substrates, (c) non-injurious to surface coatings, (d) quick setting.

In practice the choice is limited and only three adhesive systems have been found to have most of the properties required, although all are deficient in some respect. A liquid epoxide resin/amine hardener (*Araldite MY 735/HY 951*) and the same resin used in conjunction with a polyamide hardener (*Araldite MY 735/Versamid 125*) met all requirements other than the desired speed of setting, although it was found necessary to allow the mixed resin and amine hardener to age for 30 minutes before use in order to avoid attack on the paint. For all determinations other than on vertical surfaces the epoxide adhesives were adequate. On vertical surfaces, however, it was found that the specimens slipped and became detached before the adhesive set and it was not always practicable to secure them. In all determinations on vertical surfaces *Eastman Kodak 910*, a mixture of alkyl  $\alpha$  cyanoacrylates thickened with some polymeric  $\alpha$  cyanoacrylates, which sets by the base catalysed addition polymerisation of the cyanoacrylate monomers, was used. However, this system caused attack on certain surface coatings, notably relatively young films of those paints drying by an oxidative mechanism, and therefore had limited applicability.

When attack on the coating was thought to be likely the amine cured epoxide adhesive was used, in spite of the practical difficulties associated with its use. The short setting time of the *Eastman Kodak 910* (1-2 minutes under normal

ambient conditions) enabled specimens to be bonded to any test surface without the need to hold them in place during a prolonged period, and the test could be carried out within 2-4 hours. This was of particular value when the effect of high humidity or water or adhesion was being investigated.

To carry out an adhesion measurement by the torque method the surface was cleaned free of grease or surface water, and where pronounced chalking had occurred the surface was lightly abraded. The test was normally carried out using five specimens, which were bonded to the test surface with the chosen adhesive. After allowing to cure for 2-3 hours in the case of the cyanoacrylate adhesive, or 16-24 hours for the epoxide adhesives, the specimens were twisted off using the supporting table and torque spanner. This is illustrated in Fig. 3.

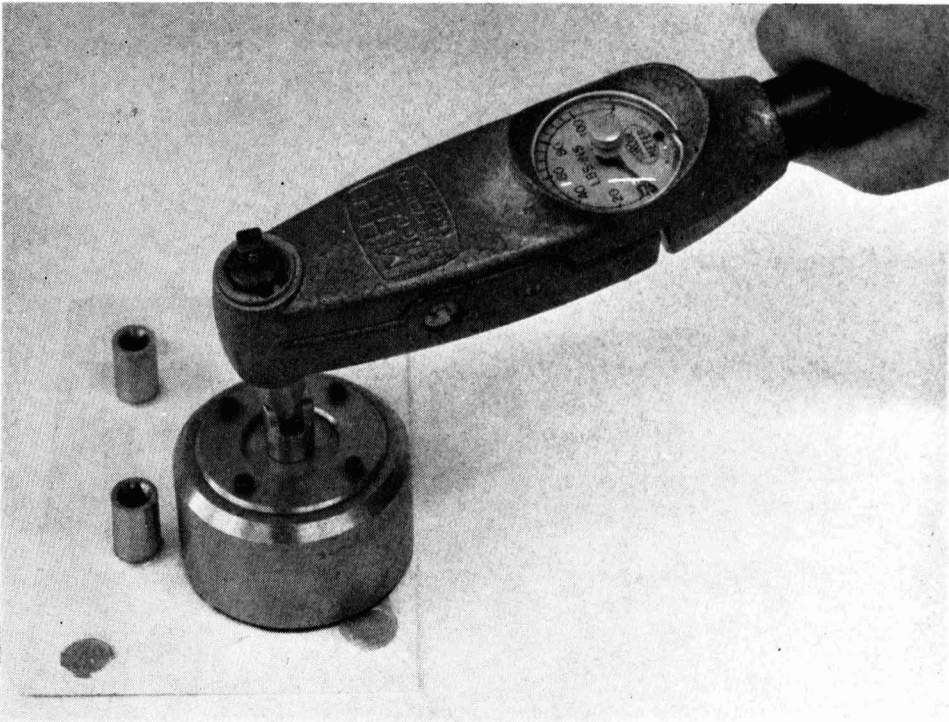


FIG. 3. THE TORQUE TEST DETERMINATION

## RESULTS

### Adhesion of Coatings in Service

In order to establish that the Torque Test was a practical method suitable for use under any envisaged condition, the majority of determinations were carried out on coated objects in daily use. In addition some direct comparisons between the torque method and the "Sandwich Method" were carried out on laboratory prepared panels.

Typical values obtained from the Torque Test are given in Table II.

TABLE II  
ADHESION VALUES OF VARIOUS COATINGS—TYPE D SPECIMENS

Coating and age	Substrate	Position	Mean torque value lb in	Calculated* mean adhesion psi	Adhesion* range psi
Alkyd paint to DEF 1052 (two years) .. ..	Wood	Vertical, exterior	30	1,200	1,120-1,240
As above under wet conditions .. ..	Wood	Vertical, exterior	10.5	420	360-460
Grey alkyd paint, age and composition unknown	Aluminium	Vertical, exterior	50	2,000	1,840-2,160
Cream tung oil/phenolic paint (18 months) ..	Mild steel	Vertical, interior	74	2,950	2,600-3,160
Grey alkyd paint (four years) .. ..	Asbestos	Horizontal, interior	100	4,000	3,800-4,200
Cream stoving paint, age and composition unknown .. ..	Tin plate	Horizontal, interior	67.5	2,700	2,520-2,800
Pva emulsion paint (three years) .. ..	Brickwork	Vertical, interior	23	920	600-1,100
Micaceous iron oxide (two years) .. ..	Galvanised	Vertical, exterior	46.2	1,850	1,680-1,960
As above under wet conditions .. ..	Galvanised	Vertical, exterior	8.5	340	240-380
Proprietary aluminium paint (five years) ..	Aluminium	Horizontal, interior	22.2	890	880-1,000

\*Calculations based on the assumptions made in Section 3.

In general the results obtained were reproducible, particularly when the coating under test had been applied to surfaces on which a good standard of surface preparation could be anticipated and when the determinations had been made indoors. Thus variations in ambient humidity were reflected in changes in the values obtained, and repeat experiments, although producing

only a small scatter in individual tests, showed a considerable difference in the mean value.

Reference to Table II will show that the test appears to give fair reproducibility over the whole range of adhesion values from 400-4,000 psi on a variety of substrates. Although quoted as adhesion values, some of the determinations represent cohesion failures, or failures within the system rather than at the paint/metal interface. In spite of this the values can be regarded as a measure of the strength of the weakest point in the system.

Similar tests in which the type *A*, *B* and *C* specimens were bonded to the coated surfaces showed that the adhesion value measured was frequently lower than the values obtained from the identical coating using the type *D* specimens. This was particularly noticeable when *Eastman 910* was used as the adhesive on vertical surfaces. This was attributed to the difficulty experienced in bonding the entire area of the specimen to the coating, due to brushmarks, surface defects, etc., and the lack of gap-filling properties characteristic of the adhesive. In tests carried out on laboratory prepared panels using an epoxide adhesive, little difference in the mean values due to specimen configuration was observed. The results of these tests are shown in Table III.

TABLE III  
MEAN TORQUE VALUES FROM SPECIMENS *A*, *B*, *C* AND *D* (LB IN)

Coating and substrate	Type <i>A</i>	Type <i>B</i>	Type <i>C</i>	Type <i>D</i>
Polyurethane/etch primer on aluminium ..	89	86	102	99
Polyamide cured epoxide on aluminium ..	54	52	58	56
Polyamide cured epoxide on mild steel ..	93	88	93.5	95

Although in theory it may seem advantageous to use annular specimens, there is no practical advantage to be gained. The annular specimens are also more costly to manufacture than the solid cylindrical specimens and are particularly susceptible to mechanical damage, either during use or subsequent cleaning.

#### Comparison of Torque and Sandwich Test Adhesion Values

Tests were carried out on selected paint systems applied under laboratory conditions to carefully prepared substrates, the adhesion being measured by the two test methods at the same stage of cure. The values obtained are shown in Table IV.

The results calculated from the torque test are generally significantly lower than those indicated in the sandwich technique, but a calculation shows that the ratio of torque test value to sandwich test value falls in the range 1.1-1.2 in every determination carried out. Further work would be necessary to establish whether this was invariably the case, but if this were shown to be true it would enable a direct comparison of results obtained by either test method to be made.

TABLE IV  
COMPARISON OF TORQUE AND SANDWICH METHOD RESULTS—TYPE D SPECIMENS

Test coatings	Torque test			Sandwich test	
	Mean torque value lb in	Calculated mean adhesion psi	Coefficient of variation	Mean adhesion psi	Coefficient of variation
White polyurethane two-pack system on aluminium .. .. .	67.5	2,700	9.1	3,150	5.0
As above with etch primer	97.5	3,900	6.3	4,750	4.1
Polyamide cured epoxide mild steel .. .. .	90.0	3,600	8.2	4,160	3.7
Long oil alkyd on tin-plate .. .. .	46.5*	1,980	4.5	2,300*	8.9
Chlorinated rubber paint on mild steel .. .. .	71.5	2,860	10.4	3,400*	12.1

\*denotes cohesion value.

During the tests shown in Table IV an area of the aluminium panel to which the etch primer and polyurethane coating were applied was deliberately left uncoated with etch primer, the polyurethane coating being applied overall. It proved possible to establish the position of this uncoated area by means of the Torque Test.

#### PROBABLE SOURCES OF ERROR IN TEST METHOD

##### Errors Due to Tolerances

Tolerances of  $\pm 0.001$  in were applied to all specimen diameters, and on the assumption that the diameters were maintained exactly at the shearing face, values for stresses actually produced by a maximum torque of 120 lb in were calculated. Extreme dimensions were used for calculation.

From Table V it can be seen that the errors introduced from this source are low for the solid cylindrical specimens and can be ignored. The errors in dimensional tolerances in the ring specimens are very much greater, and for types C and D are significant.

##### Errors Due to Torque Spanner

In a new instrument the difference between applied and indicated torque is likely to be small and can probably be neglected. Where the instrument has been in service for some time the error may be very much larger, and periodic calibration should be carried out, as it may be significant at low shear stresses.

TABLE V  
 ERRORS DUE TO EXTREME DIMENSIONS OF TEST SPECIMENS

Type	$D_0$	$D_i$	Calculated stress at 120 lb in (psi)	Percentage variation of 4,800 psi
A	0.502 0.504	— —	4,820 4,770	1.2
B	0.519 0.521	0.289 0.287	4,860 4,760	2.1
C	0.749 0.751	0.686 0.684	4,960 4,580	7.9
D	0.999 1.001	0.967 0.965	5,160 4,600	11.6

### Errors Due to Faulty Technique

Errors due to faulty technique are difficult to estimate or assess and probably lie in the application of varying shear rates throughout the separate determinations. This is largely a matter of technique and can be controlled as the operator becomes more practised. Errors due to the introduction of a peel component in the stress applied appear to be small when the supporting table and universal joint are used. In experiments carried out during the development of this test method, the torque was applied by tilting the torque meter at angles up to 30° from the horizontal, without materially increasing the scatter of results.

It is probable that the variations in adhesion or cohesive strength, due to variations in surface preparation, contamination, or composition, thickness and cure of the applied coating, are the major cause of variability in the result.

### CONCLUSIONS

It is considered that the Torque Test holds considerable promise for the determination of the adhesion of surface coatings in service, being relatively inexpensive and acceptably reproducible. Although it is destructive to the coating system over small areas, it is non-destructive to the substrate, and may be applied to any object or component having a plane surface of a few square inches. The method is sensitive enough to distinguish between the adhesion of paint systems in the dry state, and when water-soaked, and the presence or absence of surface preparation or pretreatments.

It should find ready use in the investigation of surface coating complaints, since the adhesion can be determined precisely under the actual service conditions on the defective component. It may be used for assessing surface cleanliness, degree of cure or presence of the stipulated coats of paint, and may find use as a routine control tool.

[Received 17 April 1964]

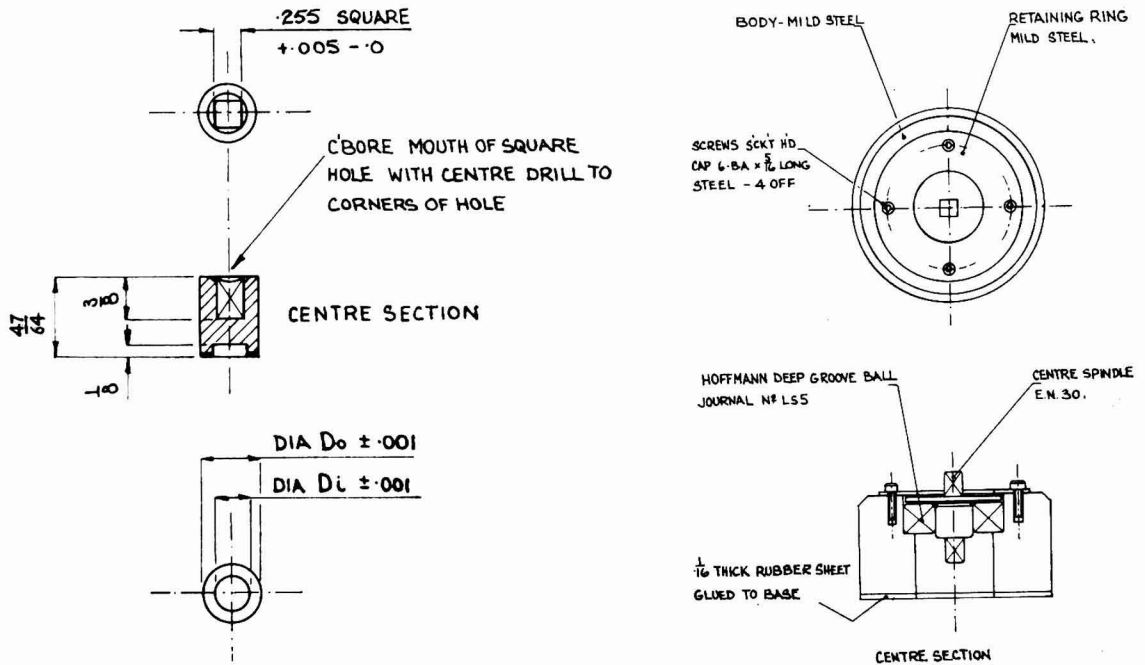
REFERENCES

1. JOCCA, 1963, 46.4. Paper submitted by the Joint Services R and D Committee.
2. Corrosion Technology, 1963, 10, 195.

ACKNOWLEDGEMENTS

The authors wish to thank the Director, AWRE, for permission to publish this paper, and to acknowledge the assistance of Mr. J. H. Tidy in the engineering aspects of this work.

APPENDIX



SKETCHES OF, LEFT, THE SPECIMENS AND RIGHT, THE SUPPORTING TABLE



# Queensland Health Law in Relation to Paint and Related Products\*

By M. H. GABRIEL

*Department of Health and Home Affairs, Brisbane*

## INTRODUCTION

The law relating to paint in Queensland is probably more extensive and detailed than in any other Australian State. Perhaps representatives of paint manufacturing industries may be more inclined to use the term restrictive. However, like most other health laws, the laws relating to paint have come into being for the sole purpose of protecting the public and have not been framed with any intention to harass the trade.

Queensland lies between 11° and 29° latitude south and is therefore tropical and sub-tropical. Until recently the vast majority of buildings were constructed of wood, a circumstance which was not surprising considering the plentiful supply and cheapness of a large variety of hard, soft and decorative woods available.

As a result of the extensive use of wood externally, a great deal of paint was and still is used for protection and decoration, and, as a result of the heat, extreme actinic activity of sunlight and the moist conditions which prevail in many areas, deterioration of paint is quite rapid.

White lead was formerly the basis of most house paints and deterioration of white lead paints leaves a powdery coating very rich in soluble lead. As far back as 1897 lead poisoning in children was a frequent occurrence in Queensland, but at first paint was not recognised as the source of the lead. In 1904, Dr. Lockhart-Gibson recognised painted railings and exposed walls as the source of lead in many of the cases and, following on this, supporting evidence began to accumulate. By 1922 the Queensland branch of the British Medical Association endorsed the work of the pioneers and regarded legislation against lead as essential.

Anyone interested in this subject should take the trouble to read a very interesting brief account entitled *The History of Lead in Queensland*, by Dr. E. M. Rathus, which was published as Appendix A (page 114) of the annual report of the Health and Medical Services of the State of Queensland for the year 1957-58.

## THE LEGISLATION

In September 1922 a Bill to amend the Health Act was introduced. Clause 29 of this Bill provides that :

No paint containing more than 5 per cent of soluble white lead shall be used within 4 ft of the ground or floor of any residence, hall, school or other building to which children under the age of 14 years have access, or any verandah, railing, gate or fence. No surface paint which contains more than 5 per cent of soluble lead shall be rubbed down in a dry condition.

---

\*Presented to the Fifth Australian Convention held at Warburton from 13-16 June 1963.

This Bill was proclaimed on 1 July 1923 and was the basis of most of the legislation for many years.

In January 1956 white lead was totally banned as a paint pigment by an amendment to the Health Acts, 1937 to 1949.

Since 1924 the Queensland Works Department has used only lead-free paints on their buildings, and since 1954 the Railway Department has followed suit in so far as its wooden buildings have been concerned.

### Summary of the Important Factors

Now consider the law as it stands at the moment. It is not intended to set out the law as it is in the statutes since anyone who wants the details can make a study of the Acts and Regulations themselves, but a précis will be given here.

The legislation on which all of the paint law rests is *The Health Acts, 1937 to 1962*, which is current at the moment. Several sections deal directly or indirectly with paint.

*Section 5* includes a definition of paint which may be of interest :

PAINT—Without limiting the ordinary meaning, includes any substance of any kind whatsoever used or intended to be used for application as a colouring or protective coating to any surface : the term includes oil paint, water paint, enamel and distemper, and any substance of any kind whatsoever used in the composition of any paint.

*Section 127* is the principal section dealing with paint and it is essentially concerned with lead. It opens by declaring quite categorically :

(1) A person shall not manufacture, sell or use any paint containing basic carbonate white lead.

This section also prohibits the use of paint containing any lead on the roof of any type of building, any exterior surface of a building, any fence or gate, any interior portion of a house, any household furniture.

It would also be appropriate at this point to draw attention to *Section 124* which, amongst a great many other things, prohibits the use of paints containing any lead on toys and a range of other articles.

It might be added at this point that the Act defines a house as follows :

HOUSE—Includes a school, also a factory or shearing or wool shed or tent, and any other building or structure in which persons dwell or are employed : the term also includes any houseboat and any vessel lying in any river, harbour, or other water within the territorial waters of Queensland other than a vessel which is under the command or charge of any officer bearing Her Majesty's commission, or which belongs to the Government of any foreign State.

Thus it will be appreciated that the prohibition of the use of lead paints is extensive.

This same section empowers an officer to remove samples for analysis of either the dried paint on a building or of the paint being used to paint any of the structures already listed, and extends this same power to an officer of a local authority.

Further than this the Director-General of Health and Medical Services can issue an order requiring the removal to his satisfaction of paint applied in contravention of the law.

*Section 128* is the one requiring every package of paint to carry details of :

- (a) The trade name or description.
- (b) Net weight or true measure or volume.
- (c) Name and address of the maker or vendor.
- (d) A statement of the ingredients in percentage proportions.

*Section 129* deals with the quality of paint used by a contractor in painting a building for another person. The principal clause reads :

Where any person (herein called "the Contractor") undertakes or contracts with another person to paint any premises owned or occupied by such other person, such contractor shall not, without the knowledge and consent of such other person, use in the mixing and/or application of such paint any barytes or whiting or other deleterious substance or ingredient of inferior quality.

In addition to the provisions in the Health Acts, *The Paint Regulations of 1954* also apply. Many of the provisions of these regulations have been superseded by later amendments to the Act, and in fact amended paint regulations are pending. Nevertheless the regulations still have the force of law and many of the provisions will be of interest, so the principal measures not already dealt with in connection with the Act will be briefly outlined.

### **The Labelling of Products**

With regard to labels, the Regulations call for all of the details required by the Act, but go further by specifying that the statement of composition shall be printed so as to afford a distinct colour contrast to the background. In addition, the label shall not, by any statement, claim, design, device, fancy name or abbreviation, mislead the purchaser concerning the paint or any of its ingredients.

It has already been seen that white lead is completely banned, but the manufacture and sale of paints containing other lead compounds is not banned. However, their use is restricted as previously indicated under the provisions of the Act, and their labelling is covered by sections of the Regulations. Paints containing red lead and lead chromate have to show on the label, in addition to the percentage composition, the percentage of soluble lead in one of several prescribed ways.

Certain standards are also prescribed for paints described by the names :

- (a) Genuine white zinc paste or white zinc in oil,
- (b) Zinc paint,
- (c) Ferric oxide paint,
- (d) Roof paint,

and, in addition, a paint must be described as "barium sulphate mixed paint" if it contains more than 50 per cent of barium sulphate, and this name must be prominently shown on the label as the main description of the paint.

Some ingredients must be declared by the names prescribed. These are :

- (i) Barium sulphate,
- (ii) Calcium carbonate,
- (iii) Clay or argillaceous material,

- (iv) Ferric (or iron) oxide, red oxide or red oxide of iron,
- (v) Lead chromate,
- (vi) Silicious material,

but lithopone may be described by that name.

There are yet other provisions of the law which have to do with paints since certain paints and allied products come within the scope of *The Poisons Regulations of 1958*. One section, Regulation 66, reads :

No person shall sell any chalks, pencils, crayons, school pastels, finger colours, show-card colours, and poster paints which contain any poison. Nor shall any person sell any pencil of any type whatsoever which contains any poison in the outside lacquer of such pencil.

While the onus is clearly on the person selling these articles, the manufacturer must be involved ultimately. The "poison" most commonly encountered is lead, but arsenic, copper, selenium and others have been found from time to time.

Difficulty has been encountered by professional artists in securing the wide range of colours required in their work and it is possible that provision may be made in the future for such paints to contain poisonous substances, provided that they are included in a poisons schedule and labelled accordingly. It would be anticipated that the price of the paints and the poison labelling would be against their purchase and use by children.

Antifungal paints can escape the labelling requirements of the Poisons Regulations if the proportions of the active ingredients fall below the set tolerances, which are : (a) pentachlorophenol and its salts 0.25 per cent, (b) mercury compounds 0.2 per cent, (c) phenol 0.2 per cent, but all must be correctly declared on the label. These and other tolerances are under review at the moment, and in the light of present practice and requirements some relaxation can be expected shortly.

Another interesting case is that of automotive finishes and retouching paints. These can contain up to 3 per cent of antimony oxide without having to be labelled poison, but of course the presence of this ingredient must be correctly shown in the statement of composition. Insecticidal paints seem to have gone out of fashion, but tolerances of up to 10 per cent of DDT, etc., are still allowable.

This by no means exhausts the list of paints and paint ingredients which may come within the scope of the Poisons Regulations, but some idea may have been gained of the problems which arise from the public health point of view.

Finally, one of the more recent Regulations, namely "The Dangerous Substances Regulations of 1961," must be mentioned. Packs of less than one gallon of many volatile petroleum derivatives (including mineral turpentine), of methylated spirits, oil of turpentine or mixtures of these, of lacquer thinners, etc., are required to be packed in special types of container and specially labelled. The list of substances included in these Regulations is fully set out in the law and should be studied.

## CONCLUSION

In conclusion, it must be pointed out that only the essential features of the law as it touches on paint and related products have been given here, and it must be impressed that the Queensland Health Department is willing at all times to clarify any points of its law for the guidance of manufacturers and packers and to comment on any labelling proposed to be used on any product. There is, therefore, no need to involve principals in expensive packing, printing and labelling which may be quite unacceptable in Queensland. Upon receipt of details of the composition of the product, the proposed packaging and the proposed labelling, the Department will be quite happy to advise.

*[Received 13 May 1964]*

## DISCUSSION

MR. H. A. MACDONALD asked if Dr. Gabriel would comment on the up-to-date position with regard to the use of poisons in underwater ships' paints, for example, anti-fouling.

DR. GABRIEL replied that paints for use below the water-line on boats and ships fell in either the red-lead group or the anti-fouling group. The latter generally contained mercury or copper compounds and very occasionally even copper arsenide. The Department took the attitude that these were not normally accessible to children and others likely to be accidentally poisoned. As long as the containers were correctly labelled the protection of the users of these paints was left to the Division of Industrial Medicine and the Department of Labour and Industry.

MR. MACDONALD also asked for comment on the position where a firm or company in another State might have a contract for preparing structural steel, for example, for use in Queensland for building a factory, and it was shop primed with a red-lead primer.

DR. GABRIEL said that there was no ban on the manufacture, sale and use of red-lead paints even within Queensland, provided they were correctly labelled and were not used in the situations specifically prohibited by the law. In point of fact, a great deal of red lead was used on railway bridges and for the protection of points and cross-overs after manufacture. It was a question of ease with which persons likely to be accidentally poisoned could get to the paint. He might mention one interesting case where red lead was used to protect the structural steel in a bulk sugar terminal building. It was felt that there was little harm being done and the likelihood of contamination of the sugar was very remote, but the Department suggested that future structures should be primed with an aluminium powder-based paint or a bitumastic paint to be quite sure of freedom from lead. The greatest danger with red-lead paints arose when old, deteriorated paint had to be removed, but this was an industrial medical matter and was kept under constant surveillance.

MR. E. V. COLLINS said that he had been most interested in the talk, and he was one who had battled his way through the regulations for many years endeavouring to comply and to follow the many sub-clauses. There were two things that had occurred to him: (a) Would it be possible, or had Dr. Gabriel's Department already put out some kind of general guide for paint formulators in order that these things could be more readily understood so that time and misunderstandings could be avoided. Unfortunately many of the formal Government regulations were rather involved documents and many took a long time to acquire the necessary legal insight to be absolutely certain that the paint complied with the regulations. (b) The other thing

that he would like to mention was that since children in Queensland appeared to be growing up in a particularly hazardous environment, and the high actinic light factor which made paints break down, and could, if these paints were dangerously formulated, give rise to lead poisoning. Under these circumstances, had the Queensland Health Department prepared or offered lectures to schools and other organisations that had contact with young people on the dangers of their environment to children and had they drawn to the attention of schools and the teachers, etc., the implications of dimpled bottles, and the little tags and warnings that were required to be placed on containers.

DR. GABRIEL, on the question of publishing a brief outline of the law for the guidance of manufacturers and others, the Department had produced a two-page set of notes some years ago, but these were now out of date. Experience showed that it did not help very much, since all of the *detail* of the law had to be known and carefully applied to each specific case. The best arrangement was for a manufacturer to submit his plans and proposals to the Department, who were always ready to advise him on exactly how to pack and label any particular product in conformity with the law.

Concerning the second part of the question, Dr. Gabriel could not say that anything had been produced exactly as was suggested, but in a book for teachers entitled *Subject Health* there was a great deal on poisoning and accidental dangers. The Queensland Health Education Council had also issued a great many pamphlets dealing with accidents, hazards and poisoning, but he felt personally that health and safety subjects generally deserved to be given more prominence in the school curriculum.

MR. E. G. FLETCHER referred to a case that had just arisen in Western Australia involving the use of hazardous paints, about which he would be very interested to hear Dr. Gabriel's comments. The Western Australian Government Railways, following a certain amount of union pressure, had introduced a complete and total ban on the use of lead in any paint which had to be sprayed; this ban extended to lead driers as well as lead pigments. Unfortunately a colour that was used in some quantity was British Standard Colour 356—golden yellow—and had presented problems in trying to produce a satisfactory golden yellow without the use of lead chromate. The industry brought this to the attention of the railways and they claimed that the hazard in such a paint was not absorption into the stomach, where a paint containing less than 1 per cent lead would be satisfactory, but inhalation into the lungs, and this was the principal reason for introducing the total ban. Mr. Fletcher said he would be very interested to hear Dr. Gabriel's comments on the actual hazard of the inhalation of a paint containing less than 1 per cent soluble lead. The second part of the question related to the drier combinations; they insisted on using a zirconium octoate, and it occurred to Mr. Fletcher that zirconium in itself might be just as hazardous as lead when inhaled.

DR. GABRIEL said that the application of paints by spray methods was left entirely to the Division of Industrial Medicine and the Department of Labour and Industry. The latter Department administered legislation in connection with the proper ventilation of spray booths, protective clothing, masks, etc. Unless a process was shown to be a health hazard to which children or the public at large were exposed, his Department did not have the power to interfere. With respect to lead driers, the presence of these in paint was allowed, as also was the principle that commercial pigments might contain traces of lead. Consequently an unofficial tolerance of 1 per cent lead in paints to allow for driers and unavoidable impurities was applied. As far as he was aware, the question of the substitution of lead driers by zirconium driers had not been raised.

MR. FAUL prefaced his remarks by saying that, as a Queensland paint manufacturer, he personally had been fully convinced that the Department in Queensland was



correct in bringing in regulations controlling lead to the levels which it has. He was convinced of this by the figures which were supplied of the deaths from nephritis over past years by the Department. The point he wanted to make was the continuation of the application of the formula stickers that manufacturers were confronted with in Queensland. It was his belief that this was a continuing and unnecessary complication as far as paint manufacturing and processing was concerned. It was an additional financial burden and he suggested that it would be a mistake if the other States were considering the adoption of this idea in their application of this approach to lead control.

DR. GABRIEL could not offer any hope that the law in requiring the declaration of composition on containers would be altered. It was felt that this was most desirable both as a check on the use of lead compounds and as a means of quality control. It had been put to the Department that this requirement forced a manufacturer to disclose information which he wished to keep secret, but it had always been felt that a paint chemist could soon discover the composition of any paint marketed by a competitor. In any case the declared composition did not disclose any special method of manufacture which might be much more important than the mere ingredients; this applied to all manner of manufactured articles—foods, medicines, cosmetics, confectionery, etc. Dr. Gabriel saw trends, both here and overseas, extending the principle of declaration of composition of a wide range of preparations. This should not embarrass an ethical manufacturer and it must favourably impress the discriminating purchaser.

MR. CAMERON asked if there were any negotiations to unify the legislation throughout all the States.

DR. GABRIEL said there had been discussions for some considerable time aiming at a degree of uniformity of paint regulations throughout Australia, and at a recent meeting of the National Health and Medical Research Council a draft of proposed uniform regulations was tabled, and Dr. Gabriel said it had many good points. However, it does not go nearly far enough for the purposes in Queensland—just to mention one point, the labelling provisions were rather long and involved and yet he felt did not cover the basic requirements. The really bright spot is that a start had been made towards achieving uniformity.

MR. L. J. A. WILLIAMSON wanted to ask under what classification did calcium plumbate primers, which are now being put out for galvanised iron, come.

DR. GABRIEL said that as far as he knew calcium plumbate had not come to the Department's attention and he had to plead ignorance. He suggested that, since it was a compound of lead, it would be subject to the same restrictions as other lead compounds.

---

## ERRATUM

### HIGH SPEED MIXING EQUIPMENT

It is very much regretted that Fig. 5 on page 724 of the September issue has been inverted, and apologies are extended to the author, Mr. G. R. Lester.



## Correspondence

### LEACHING OF TOXIC PIGMENTS FROM CONTACT LEACHING ANTIFOULING PAINTS

Contact leaching antifouling paints have been defined as paints which contain sufficient toxic pigment, usually cuprous oxide, for direct contact to occur between the toxic particles within the paint film. As one particle dissolves another in contact with it is exposed to solvent action. It has been proposed by Ferry and Ketchum (*Ind. Eng. Chem.*, 1946, **38**, 806) that the gradual fall in leaching rate with time, referred to as the steady state leaching period, reflects the exhaustion of "chains" of particle to particle contact within the paint film, it being assumed that not every particle is in contact with others. In the course of an investigation into the natural sea water and sodium glycinate accelerated leaching rates (*JOCCA*, 1964, **47**, 323) of contact leaching paints based on unplasticised vinyl resins with a cuprous oxide volume content in the dry paint film of approximately 45 per cent, it was found that complete exhaustion of the cuprous oxide occurred even when paint films as thick as 0.003 in were employed. When partially exhausted films of these paints were sectioned and examined microscopically, a sharp boundary was seen between the unleached and leached paint matrix and there was no evidence of any cuprous oxide particles remaining in the latter. Therefore Ferry and Ketchum's theory does not apply to cuprous oxide/vinyl resin paints with toxic pigment volume contents of 45 per cent and greater. It is probable that all contact leaching paints will have a limiting value for the pigment volume content above which complete solution of the pigment will occur. Below this value Ferry and Ketchum's suggested mechanism could be a contributing factor in determining the leaching characteristics of the paint.

In the theory now proposed it is postulated that at toxic pigment volume contents above a limiting value the "steady state" leaching rate under constant external conditions is dependent only upon the solubility of the pigment and its rate of diffusion through both the exhausted matrix and the laminar sub-layer of leaching solution in contact with the paint surface. An equation has been developed relating these factors to the physical properties of the paint film and its environment. The following major assumptions have been made in deriving the equation: the Stokes-Einstein equation for diffusion is obeyed; the toxic particles are spherical and uniformly distributed in the paint film; the toxic material does not undergo chemical change in solution; the exhausted matrix remains intact; the leaching solution contains none of the dissolved toxic pigment; the paint vehicle wets the toxic particles and the thin film between toxic particles exhibits brittle fracture under stress. The equation derived is of the form:

$$F = \frac{kK' V S T}{(L + nKR) r \eta} \dots\dots\dots 1$$

$$P$$

where  $F$  is the toxic release rate from the film,  $V$  is the volume fraction of toxic pigment in the film,  $S$  is a parameter dependent upon the solubility of the pigment in the leaching solution,  $P$  is a parameter dependent on the

arrangement of the toxic particles in the paint film, which will vary with  $V$ ,  $K$  and  $K'$  are parameters dependent on the physical properties of the paint film,  $T$  is the absolute temperature,  $L$  is the thickness of the laminar sub-layer of leachate contacting the surface of the film,  $n$  is the number of "layers" of toxic pigment particles already leached from the film,  $R$  is the radius of the toxic particle,  $\eta$  is the viscosity of the leaching solution,  $r$  is the effective radius of the toxic ion or molecule in the solvent and  $k$  is a constant. For a given paint film leached under uniform conditions,  $nR$  is directly proportional to  $D$ , the thickness of the exhausted portion of the film, and the equation reduces to :

$$F = \frac{A}{L + CD} \approx \frac{A}{10 + CD}$$

where  $A$  and  $C$  are constants and the laminar sub-layer thickness for turbulent conditions is assumed to be 10 microns (Ragg, *Farbe und Lack*, 1952, 88, 99). The mathematical treatment could be extended to systems containing more than one soluble pigment, or containing insoluble extenders.

Fig. 1 shows experimentally determined leaching rates of copper from three vinyl antifouling paints based on an unplasticised vinyl resin with toxic volume contents of 74.0 per cent, 68.0 per cent and 52.3 per cent of cuprous oxide, leached in 0.025 M sodium glycinate : 0.48 M sodium chloride solution plotted as individual points against the thickness of the exhausted paint matrix (calculated from the total loss of copper from the paint film). The constants  $A$  and  $C$  were determined for each of these paints by substituting experimental steady state leaching values in the above equation. The values obtained for

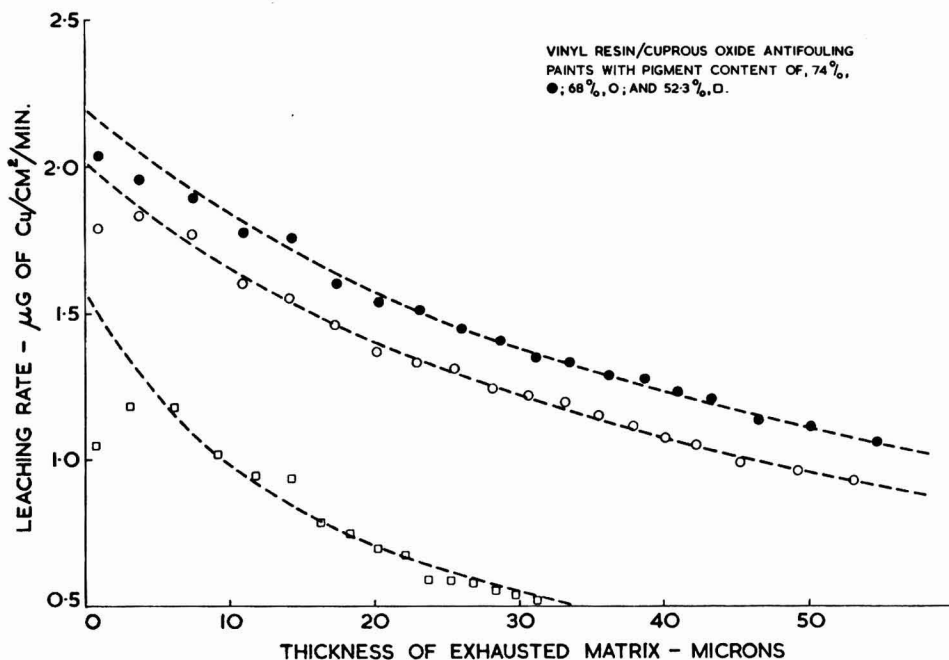


FIG. 1. LEACHING RATE AS A FUNCTION OF EXHAUSTED MATRIX THICKNESS

A were 22.0, 20.2 and 15.6, and for C, 0.197, 0.221 and 0.60 in order of decreasing PVC. The shape of the calculated leaching rate curves based on these constants shown as broken lines in Fig. 1 agrees closely with the experimental data over the steady state leaching period, indicating that the form of equation 1 may be correct. The theory provides that the initial steady state leaching rate should be directly proportional to the toxic pigment concentration. The values of the pvc divided by initial calculated leaching rates for the paints are 33.6, 33.7 and 33.5 in order of decreasing PVC, giving some further evidence that the form of the equation may be correct.

The major temperature dependent terms in equation 1 can be compared with the sea water leaching rates at various temperatures of two contact leaching cuprous oxide based paints determined by Ferry and Carritt (*Ind. Eng. Chem.*, 1946, **38**, 612), who concluded that the main rate determining step in the dissolution of these paints is the formation of  $\text{CuCl}_2^-$ . Under the conditions of the determination  $n$  would be small compared with  $L$  and the equation can be written as :

$$F = \frac{kK' V S P T}{L r \eta}$$

the major temperature dependent terms are  $\eta$  and  $L$ , the latter being proportional to  $\eta^{\frac{1}{2}}$  (Landweber, *Trans. Soc. Naval Architects and Marine Engineers*, 1953, **61**, 5). The leaching rate is therefore directly proportional to  $T/\eta^{3/2}$ . Fig. 2 shows the log of  $T/\eta^{3/2}$  and the log of the measured leaching rates of the two paints, the latter converted to suitable scales for comparison purposes, plotted against the reciprocal absolute temperature. Ferry and Carritt conclude that

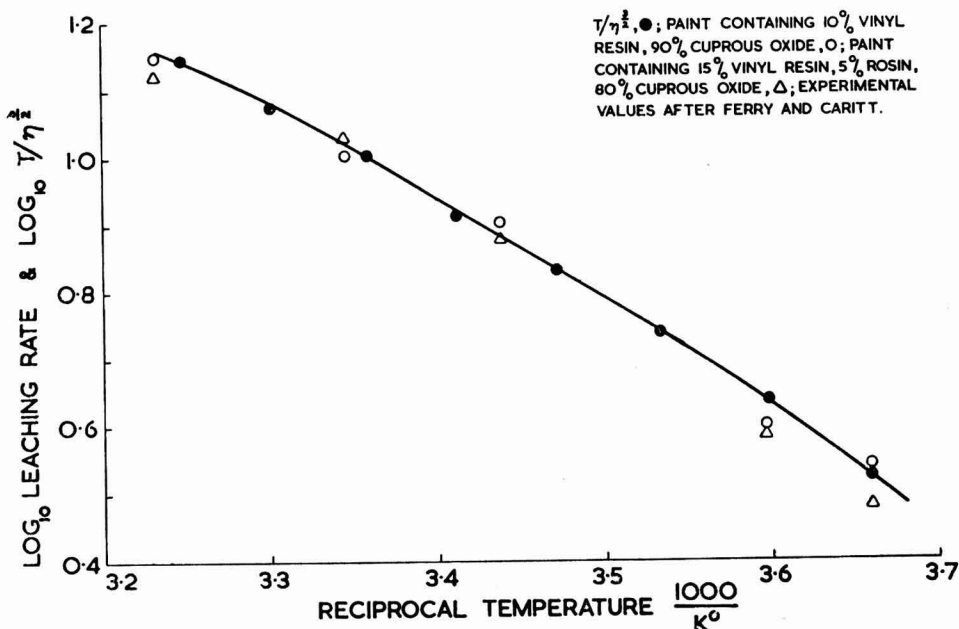


FIG. 2. LEACHING RATE AND MAJOR TEMPERATURE DEPENDENT TERMS IN EQUATION 1 AS A FUNCTION OF TEMPERATURE

the slope of the two curves, which approximate to straight lines, represents an activation energy of 12,000 calories for the dissolution of cuprous oxide indicating that diffusion is not limiting the solution rate under these conditions. The curve for  $T/\eta^{3/2}$ , which is dependent solely on diffusion, gives the same slope and close agreement with the experimental points. It therefore appears probable that for cuprous oxide based contact leaching paints, the factor controlling the leaching rate is the rate of diffusion of the toxic material through the exhausted matrix and the sub-laminar layer, and that the rate of formation of the  $\text{CuCl}_2^-$  ions can be only of minor, if any, importance. It is hoped to publish complete details of this hypothesis, when the experimental determinations at present being carried out to assess the validity of the assumptions made in the derivation of the equation are completed, and the values of at least some of the parameters involved have been established.

This work forms part of a programme sponsored by the Department of the Navy, and this letter is published by permission of the Chief Scientist, Department of Supply, Australia.

F. MARSON.

*Department of Supply,  
Australian Defence Scientific Service,  
Defence Standards Laboratories,  
Maribyrnong,  
Victoria.*

[10 August 1964

#### IDENTIFICATION OF TALL OIL FATTY ACIDS

The interesting papers by Rybicka and Greaves in the July issue of the *Journal* contained some information on the fatty acid composition of tall oil (pages 487 and 505).

It was stated that there should be some uncertainty concerning some of the fatty acid components analysed by GLC.

Recently papers have been published by Finnish authors<sup>1-5</sup> which may have escaped the attention of people interested in tall oil alkyd manufacture. The papers give information on the identification of tall oil fatty acids. In our laboratory we have also done some work in this field. The following conclusions can be drawn :

The "unidentified" acid mentioned in Table I, page 487, is *cis*-5.9.12 octadecatrienoic acid, a non-yellowing isomeric linolenic acid.

In tall oil fatty acids for alkyd manufacture from Scandinavian tall oil there should be about 5 per cent conjugated linoleic acid and a few per cent higher boiling acids, chiefly *cis*-5.11.14 eicosatrienoic acid, a fatty acid with 20 carbon atoms, with properties similar to linoleic acid. On some widely used polyester (poly-diethyleneglycolsuccinate) GLC columns this trienoic  $\text{C}_{20}$  acid emerges together with saturated  $\text{C}_{22}$  acid.

We have found that these acids can be readily separated on a poly-butanediol-succinate column at 200°C where the relation of elution is 1.0/1.9/2.4 for linoleic/trienoic  $\text{C}_{20}$ /saturated  $\text{C}_{22}$  acids.

The content of saturated acids is very low in Scandinavian tall oil fatty acids used for alkyd manufacture. The most convenient analytical tool for testing the saturated acid content consists of column chromatography on  $Al_2O_3$  of the fatty acid methyl ester mercuric acetate adducts, according to Kuemmel<sup>6</sup>. This method separates the saturated acids for further testing by GLC.

Thus most of the fatty acid content of Scandinavian tall oil fatty acids for alkyds is linoleic acid and acids similar to this. The oleic acid content is in the range 30-40 per cent.

A. LUNDQUIST.

*Bergviks Hartsprodukter AB,  
Sandarne, Sweden.*

#### REFERENCES

1. Aho, Y., Harva, O., and Nikkilä, S., *Tekn. Kemian Aikakauslehti*, 1962, **19**, 390.
2. Elomaa, E., Lehtinen, T., and Alhojärvi, J., *Suomen Kemistilehti B*, 1963, **36**, 52.
3. Lehtinen, T., Elomaa, E., and Alhojärvi, J., *ibid.*, 1963, **36**, 124.
4. Lehtinen, T., Elomaa, E., and Alhojärvi, J., *ibid.*, 1963, **36**, 154.
5. Lehtinen, T., Elomaa, E., and Alhojärvi, J., *ibid.*, 1964, **37**, 27.
6. Kuemmel, D. F., *Anal. Chem.*, 1962, **34**, 1003.

## Reviews

### MANAGEMENT FOR RESEARCH AND DEVELOPMENT

By H. A. COLLINSON. Sir Isaac Pitman & Sons Ltd. Pp. viii+137. Price 16s.

The author observes that there has been a considerable increase in the number of books on management in the fields of production, selling, accounting and financial control, but little attention has been paid to the requirements of those engaged in research and development. In fact it is generally considered that normal management principles and techniques are not applicable to laboratory and laboratory work. However, the writer of the book does not agree with this, but considers that work in this field "—can and should be subjected to these basic principles and techniques."

The main difference between the operations in production and sales and in research and development is one of predictability. The operations in a production department can be predicted with great accuracy, whilst in sales departments it should be possible to predict operations with a fair degree of accuracy. In research and development departments any plans made are far less reliable, but nevertheless they can serve as valuable guides to progress.

The book is divided into chapters, a brief survey of the contents of which will give some idea of the scope of the book. In a chapter on "Research and Development Managers," consideration is given to the qualities required of personnel responsible for operating a research and development group. It is observed that as in sales departments the best salesman on the road does not necessarily make the best manager of a sales department, so in a research department the best and most brilliant bench worker does not always make the best laboratory administrator. For such a worker there should be a research ladder parallel to the administrative one which the brilliant or above average bench worker can climb more or less in step with his colleague on the administrative side.

In chapters on "Techniques for Increased Efficiency" the importance of project selection is emphasised. This selection should be made by a committee of senior managers or directors representing the major functions of the company. It should perhaps go without saying that projects selected must be ones which have reasonable chances of success and demands for resulting products must be foreseen.

If the aim of a project is to produce a new product, a clear and detailed statement of requirements, in fact a specification, must be prepared beforehand. At a certain stage in the work it may be decided that a product developed is sufficiently near to the specification requirements to be acceptable. As the author says, "Research workers are always loath to finalise a product," yet to have too long a delay in marketing can mean loss of initiative and forestalling by a competitor. On the other hand premature marketing can be disastrous.

Of direct interest to research workers affecting efficiency are salary and salary reviews, status, freedom to attend meetings, occasionally during working hours, freedom to publish articles and encouragement.

On writing reports the need to have a logical sequence is emphasised. This facilitates reading and understanding of subject matter. It is also stressed that in writing a report the type of ultimate reader must be considered. A technical report to be read by scientists and technicians would usually be quite unsuitable for managing directors.

A chapter on "Creativity, Selection and Evaluation of Personnel" deals with such aspects of staff as creativity, i.e. ability to combine known facts and ideas in a new pattern, education, experience, planning ability, knowledge in own field, ability of expression and personality.

The question of overall research expenditure of a company or group is dealt with under "Research and Development Expenditure." In this reference is made to the purchase of "know-how" from outside sources, collaboration with research associations, universities and colleges of advanced technology, private research organisations and sponsored work at research organisations.

An important chapter on "Costing Research and Development Work" advocates the need for and the value of cost budgets for research projects. Whilst such budgets cannot be accurate they can serve as very useful guides of expenditure during the course of the work.

A method for the "Evaluation of the Results of Research and Development," where this concerned the development of a new product, relies on an analysis of sales figures and trends.

A final and important chapter on the management of the small research and development unit is particularly appropriate to the United Kingdom because a substantial part of manufacturing industry is in the hands of small and medium-sized firms.

A small bibliography and short but adequate index complete a book which is well written and easy to read. It will undoubtedly be of interest and value both to technical and non-technical management.

H. G. RAINS.

### GAS CHROMATOGRAPHY ABSTRACTS 1963

By C. E. H. KNAPMAN, Editor. London : The Institute of Petroleum, 1964. Pp. 286. 1,051 Abstracts. Price 42s.

This is the sixth volume of a series which started in 1958. Many interesting papers have been abstracted in this volume. The relation between structure and gas chromatographic data was discussed (abstr. 28). Chromatographic identification of complex mixtures of high boiling compounds using GLC and thin layer chromatography has been attempted by Janak (abstr. 129). Ultramicrodetermination of chemical structure of organic compounds has been reported (abstr. 553). A combination of gas chromatography and mass spectrometry for the analysis of organic mixtures has been described by Henneberg (abstr. 569). Oxidation has been used as an aid in the identification of unsaturated hydrocarbons by gas chromatography (abstr. 608). The role of the stationary phase was discussed by Brown (abstr. 683). The relation between the composition of the mixed stationary phase and the retention time (abstr. 620). High temperature gas solid chromatography carried out at



temperatures up to 500°C has been described by Russian workers (abstr. 1), and up to 1,000°C by Americans (abstr. 68). Double column programmed temperature gas chromatography (abstr. 297). The closed loop control of continuous distillation columns by GC has been realised by Fischer (abstr. 468).

The papers of special interest to the paint industry include : GC for qualitative determination of oil content in organic coatings (abstr. 14) ; GC for tall oil and turpentine analysis (abstr. 27) ; determination of alcohols and glycols by GC (abstr. 59) ; determination of polyfunctional amines and melamines (abstr. 95) ; acrylonitrile, methyl acrylate, ethyl acrylate, methyl methacrylate separations (abstr. 231) ; plasticisers (abstr. 233) ; identification of polyhydric alcohols in synthetic resin by programmed temperature GC (abstr. 269) ; carboxylic acids in alkyd and polyester coating resins (abstr. 273) ; GC analysis of high boiling point plasticisers using a short column (abstr. 279) ; simultaneous determination of glycerol and fatty acids in glycerides (abstr. 287) ; direct analysis of solvents in lacquers by programmed temperature GC (abstr. 348) ; and separation and determination of mono-, di- and tri-pentaerythritol by programmed temperature GC (abstr. 392). Application of gas chromatography to the preparation and formulation of paint materials was discussed by Scholl (abstr. 418). Gas chromatography as a new tool for the analysis of plastics (abstr. 420). Pyrolysis-gas chromatographic technique was reported by Etre and Varadi (abstr. 507) and by Hyden (abstr. 512). Analysis of polyester resins by GC was described by Percival (abstr. 535). Collection of gas chromatographic fractions for identification by infrared spectrophotometry was described by Shearer and co-workers (abstr. 708). Uses of GLC in the field of drying oils and oleoresinous media were reported by Greaves (abstr. 727).

Constitution of fatty acids of cod liver oil was determined by DeWitt and Reed (abstr. 729). Examination of unsaturated glyceride oils by GC was reported (abstr. 731).

These examples, it is hoped, illustrate the usefulness of this publication to the workers concerned with the analysis of commercial products and raw materials.

S. M. RYBICKA.

## New South Wales Section

### THE HELIUM-NEON LASER

The lecture delivered by Dr. J. Ramsay, Division of Physics, National Standards Laboratory, was entitled "The Helium-Neon Laser."

Dr. Ramsay said that atoms could only exist in certain discrete energy states ; they might spontaneously decay from a higher state to a lower energy state with the emission of radiation whose frequency was determined by the difference in the energy levels. In the presence of radiation of this frequency two other phenomena caused by interaction of the radiation with the atom might occur. Atoms in the lower level might absorb this radiation and would proceed to the upper level and atoms in the upper level might be stimulated to emit radiation with the same frequency as the stimulating radiation and with the same phase. The lecturer then considered a beam of radiation incident on an assembly of atoms. Since the probability of absorption or stimulated emission was the same, the net result would be a loss in the beam due to absorption if there are more atoms in the lower level, whereas a gain or amplification of the beam is produced if there are more atoms in the higher level. Under normal thermal equilibrium conditions there are more atoms in the lower level, the ratio being given by

$$\frac{N_2}{N_1} = e^{- (E_2 - E_1)/RT},$$

where  $N_1$  are the number in level 1 with an energy state  $E_1$ ,  $R$  is Boltzmann's constant and  $T$  the absolute temperature.

In order to produce laser action, i.e. light amplification, there must be a population inversion so that there were more atoms in the upper level than in the lower level. The lecturer then described how this was accomplished in the case of the helium-neon laser. A mixture of helium and neon was excited by an electrical discharge. The helium atoms decayed to a metastable state where they had time to collide with ground state neon atoms. These neon atoms were then transferred directly to an upper, excited state and by this means more neon atoms could be produced in the higher state than exist in the lower state and conditions for laser action then obtain.

The excited discharge tube was then placed between mirrors having a high reflectance for the desired wavelength. These mirrors had a reflectance of approximately 99 per cent for a wavelength of 6328Å. The radiation which was reflected by the mirrors back through the tube remained in the cavity the longest time and hence was the most amplified, with the result that the emerging laser radiation was confined to a narrow beam.

The lecturer then discussed the actual procedure involved in making a laser, including the optimum mixture of helium and neon, the pressure in the tube, the optimum discharge current and the minimum length of the tube necessary for oscillation. He then demonstrated a small portable laser which had been constructed at the Division of Physics, CSIRO.

Some applications of the laser were discussed. Its application for communication was illustrated, but the lecturer emphasised that whilst its possibilities were very great in principle, there were still a lot of practical hurdles to be overcome before it would be satisfactory for use in communication.

L. J.

## Information Received

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

PLASTANOL LTD. has produced a low cost quick drying styrenated alkyd resin for industrial application. The resin, *Plastyrol S-99X*, is a rosin modified type that gives, the company claims, films of high build and gloss which are set up in six minutes and surface dry in 12 minutes.

---

The first technical bulletin (E10) describing the properties of *Epok W. 1762* water-soluble resin has just been issued by BRITISH RESIN PRODUCTS LTD. The booklet contains information about formulation, pigmentation and electrodeposition techniques.

---

### HYDROCARBON OIL DUTIES : RELIEFS OR REBATE IN RESPECT OF CERTAIN USES OF HYDROCARBON OILS

Section 6 of the Finance Act, 1964, gives the Commissioners of Customs and Excise power :

(a) To grant relief from hydrocarbon oil duty (either by duty-free delivery or by repayment of duty after use) on oils which are used as materials, solvents, etc., in the manufacture or preparation of composite products such as paints, floor coverings and rubber articles ;

(b) To allow a rebate of duty, which reduces the effective rate of duty to 2d. a gallon, on light oils such as naphtha or light distillate which are used as fuel in certain furnaces ;

(c) To approve persons as eligible to receive the relief and rebate referred to at (a) and (b) above.

In this connection, the Commissioners have now made the Hydrocarbon Oil Duties (Reliefs and Rebates) Regulations, 1964 (SI 1964, No. 1349), which take effect from 1 September 1964.

The Regulations prescribe such matters as the procedure to be followed by persons seeking approval, the conditions to be observed, the form and circumstances in which repayment may be claimed under (a) above, and the marking and colouring of the "furnace" oils under (b) above.

The Regulations also renew the 1961 provisions as to the marking of gas oil which is to be used otherwise than as road fuel, and thus replace the Hydrocarbon Oils (Marking of Gas Oil) Regulations, 1961, in this respect.

Copies of the Regulations may be obtained from HM Stationery Office, price 8d., by post 11d.

Customs Notice No. 184 sets out general information for *oil users* who are eligible for relief from duty under (a) above, and Customs Notice No. 185 gives guidance to *oil suppliers* concerning deliveries from bond of oils under both (a) and (b) above. Furnace operators who wish to receive rebated light oils under (b) above should apply to their local Officers of Customs and Excise, who will also supply copies of the Notices to traders likely to be concerned, and give further information on request.

# SEVENTEENTH TECHNICAL EXHIBITION

22nd, 23rd, 24th, 25th and 26th March, 1965

## LORD HILL TO OPEN LARGEST OCCA EXHIBITION

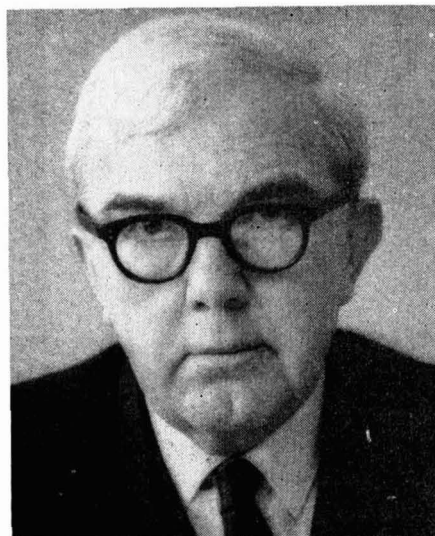
The Exhibition Committee met shortly after the closing date for applications (9 September) and allocated space to all applications received by that date. The Committee is pleased to report that the Seventeenth Technical Exhibition will cover a larger floor area than any previous Exhibition, and a particularly gratifying feature has been the considerable number of new and overseas companies who have applied for Exhibition space. A full list of the companies to whom space has been allocated is given on the following page.

The Exhibition will take place at a new venue, the Great Hall of Alexandra Palace, London, N.22, and, in order to assist those planning to visit the Exhibition a map is given overleaf, showing the various ways in which Alexandra Palace can be reached from Central London.

The map will be reproduced in each copy of the *Official Guide*, which will be sent without charge to all members of the Association early in the New Year. Copies of the *Official Guide* will also be sent individually to chemists and technologists on the Continent of Europe, to technical colleges and, through the courtesy of trade associations, to companies in the paint, printing ink and pigment industries in the United Kingdom.

The map is also being reproduced separately in a folder which gives directions in four languages French, German, (Italian and English) and copies of these will be sent with the *Official Guides* despatched to the Continent. Copies are also available to any member of the Association who wishes to send to colleagues abroad, and they will be despatched without charge upon application to the General Secretary. Following the practice of previous years, the four-language cards will be sent, together with posters, to airline companies and commercial counsellors both of British Embassies abroad and to the foreign embassies in the United Kingdom.

The total number of stands allocated for the Exhibition will be 97 and, of the companies showing, 17 have never shown at previous OCCA Technical Exhibitions, while 17 others did not show at the 1964 Exhibition. Amongst the overseas countries from which exhibits will be shown are Belgium, Denmark, France, Germany, Holland, India, Norway, Sweden, Switzerland and the United States of America.



LORD HILL OF LUTON

The Committee is pleased to report that the Rt. Hon. Lord Hill of Luton, P.C., Chairman of the Independent Television Authority and a Director of Laporte Industries Ltd., has accepted its invitation to be the Guest of Honour at the Exhibition Luncheon, which will be held at the Savoy Hotel, W.C.2. on 22 March, and to reply to the Address of Welcome by the President, Dr. J. E. Arnold. Principal officers of other scientific bodies, industrial research associations and organisations representing both suppliers and consumers will be invited to attend.

[Continued on page 844

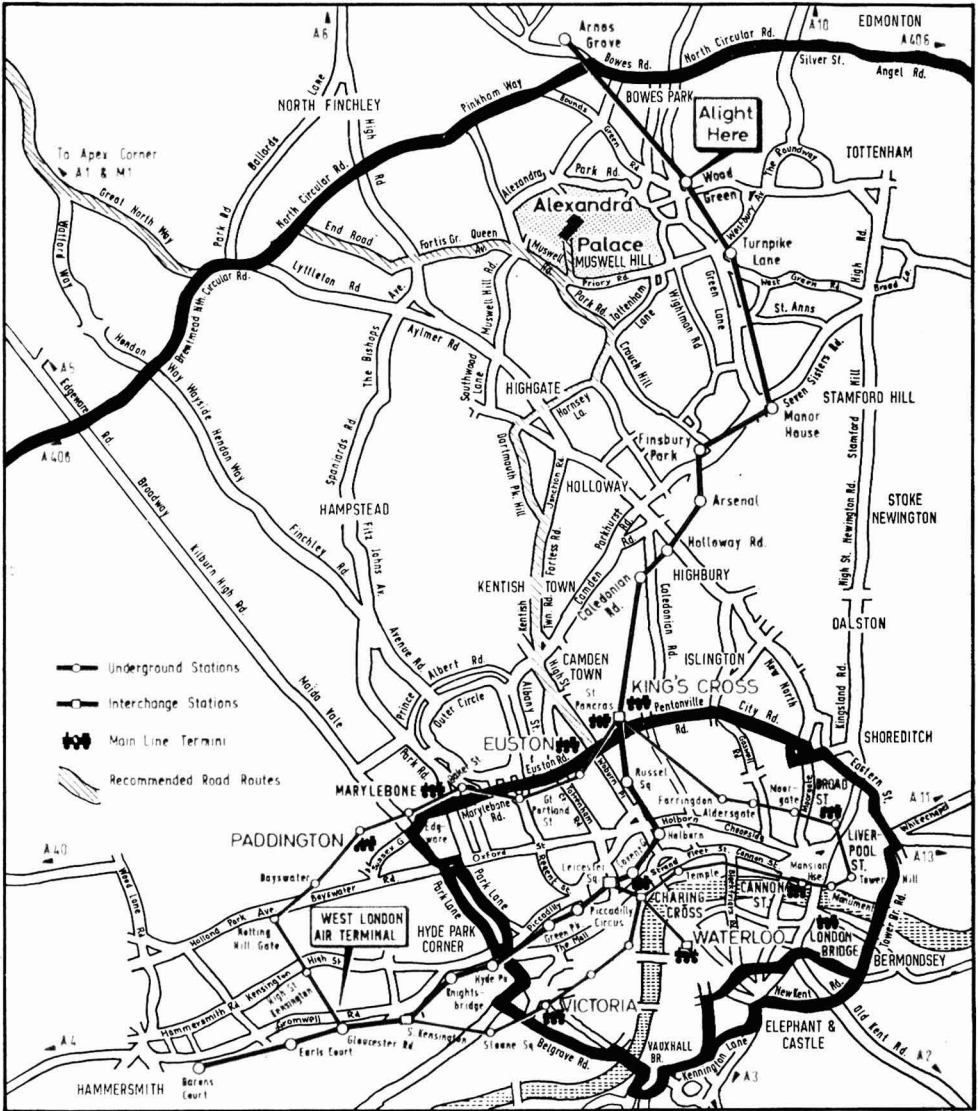
## ALPHABETICAL LIST OF EXHIBITORS AT OCCA SEVENTEENTH TECHNICAL EXHIBITION

- †Albright & Wilson (MFG) Ltd.  
 Allied Colloids Ltd.  
 Amalgamated Oxides (1939) Ltd.  
 Amoco Chemicals Corporation  
 \*Anchor Chemicals Co. Ltd.  
 Bakelite Ltd.  
 \*Beckman Instruments Ltd.  
 Berk, F. W., & Co. Ltd.  
 Bibby, J., & Sons Ltd.  
 BIP Ltd.  
 Blagden, Victor, & Co. Ltd.  
 Boehm, Fredk., Ltd.  
 Boulton, William Ltd.  
 British Celanese  
 British Oxygen Co. Ltd.  
 British Resin Products Ltd.  
 British Titan Products Co. Ltd.  
 Bush, Beach & Segner Bayley Ltd.  
 †Buhler Bros. (England) Ltd.  
 \*Byk Gulden Lomberg G.m.b.H.  
 Carless Capel & Leonard Ltd.  
 \*Chemische Industrie Synres  
 Chemische Werke Huels A.G.  
 Ciba (ARL) Ltd.  
 Ciba Clayton Ltd.  
 †Coal Products  
 †Cole, R. H., Ltd.  
 \*Compagnie Francaise Goodyear  
 \*Copley, F., & Co.  
 †Cornelius Chemical Co. Ltd.  
 †Cox's Machinery Ltd.  
 Cray Valley Products Ltd.  
 Croxton & Garry Ltd.  
 D. H. Industries Ltd.  
 \*Dispersions Ltd.  
 Dunlop Chemical Products Division  
 Farbenfabriken Bayer A.G.  
 Ferranti Ltd.  
 \*Gebruder Netzsch  
 Geigy Co. Ltd., The  
 Grampian Press Ltd.  
 Greeff, R. W., & Co. Ltd.,  
 Hardman & Holden Ltd.  
 Hercules Powder Co. Ltd.  
 †Hoechst Chemicals Ltd.  
 Imperial Chemical Industries Ltd.  
 †Imperial Smelting Corporation Ltd.  
 \*Industrial Colours Ltd.  
 †Isopad Ltd.  
 Johns-Manville Co. Ltd.  
 Kemisk Vaerk Køge A/S.  
 Kingsley and Keith (Chemicals) Ltd.  
 Kronos Titanium Pigments  
 Kunsttharsfabriek Synthese N.V.  
 Laporte Titanium Ltd.  
 Lennig Chemicals Ltd.  
 \*Little, J. H., & Co. Ltd.  
 \*Marfleet Refining Co. Ltd.  
 \*Meyer's, Rudolph, Inc.  
 †Mill Room Accessories & Chemicals Ltd.  
 Mitchell, L. A., Ltd.  
 †Mitchell, W. A., & Smith Ltd.  
 National Adhesives Ltd.  
 Nederlandse Castor Oliefabriek Necof  
 N.V.  
 \*Norsk Spraengstofindustri A/S  
 †Norwegian, Talc., A/S  
 Novadel Ltd.  
 \*Optica United Kingdom Ltd.  
*Paint, Oil & Colour Journal*  
 Paint Research Station  
 \*Pfizer Ltd.  
 Plastanol Ltd.  
 Premier Colloid Mills Ltd.  
 †Reeves & Sons Ltd.  
 Research Equipment (London) Ltd.  
 Sawell Publications Ltd.  
 Scado-Archer-Daniels N.V.  
 Sheen Instruments (Sales) Ltd.  
 Shell Chemical Co. Ltd.  
 †Shellac Export Promotion Council.  
 Silverson Machines Ltd.  
 Spelthorne Metals Ltd.  
 Steele & Cowlshaw Ltd.  
 \*Sterling Colour Co. Ltd.  
 Styrene Co-Polymers Ltd.  
 Surface Coating Synthetics Ltd.  
 †Swada (London) Ltd.  
 Titanium Intermediates Ltd.  
 Torrance & Sons Ltd.  
 †Translation & Technical Information  
 Services.  
 †United Coke & Chemicals Co. Ltd.  
 Vinyl Products Ltd.  
 \*Weyburn Engineering Co. Ltd.  
 Winkworth Machinery Ltd.

\*Denotes exhibitors who have not shown at previous Exhibitions.

†Denotes exhibitors who did not show at the 1964 Exhibition.

# 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.



*Continued from page 841]*

The Exhibition will be open for the first time on five days and the Committee feels that this arrangement will benefit companies, particularly those in the provinces and overseas wishing to arrange a rota for their technical staff to visit the Exhibition. The hours of opening will be as follows :—

Monday		
22 March	..	3 p.m. to 6.30 p.m.
Tuesday		
23 March	..	10 a.m. to 6 p.m.
Wednesday		
24 March	..	10 a.m. to 6 p.m.
Thursday		
25 March	..	10 a.m. to 6 p.m.
Friday		
26 March	..	10 a.m. to 4 p.m.

As in previous years, a stand will be devoted to Technical Education and parties of sixth form science students will be invited to attend on three mornings, when they will be given short introductory talks before touring the Exhibition. The Technical Education Stand will show the courses available in the technology of the paint,

printing ink and allied industries, and the technical careers open to new entrants.

Representatives from 30 overseas countries attended the 1964 Exhibition, and in order to assist the increasing number of both overseas visitors and exhibiting companies, interpreters will again be in attendance. There will be no charge for admission to the Exhibition, or for copies of the *Official Guide*, which will be available from the Association's Information Centre at the Exhibition or from the Association's Offices prior to the Exhibition.

Amongst the facilities available at Alexandra Palace are ample free car parking, more space for display purposes, two restaurants, together with four buffets and several bars.

Any Company or individual who wishes to receive copies of the *Official Guide* available in the New Year, should write to the General Secretary, R. H. Hamblin, M.A., F.C.I.S., F.C.C.S., Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2.

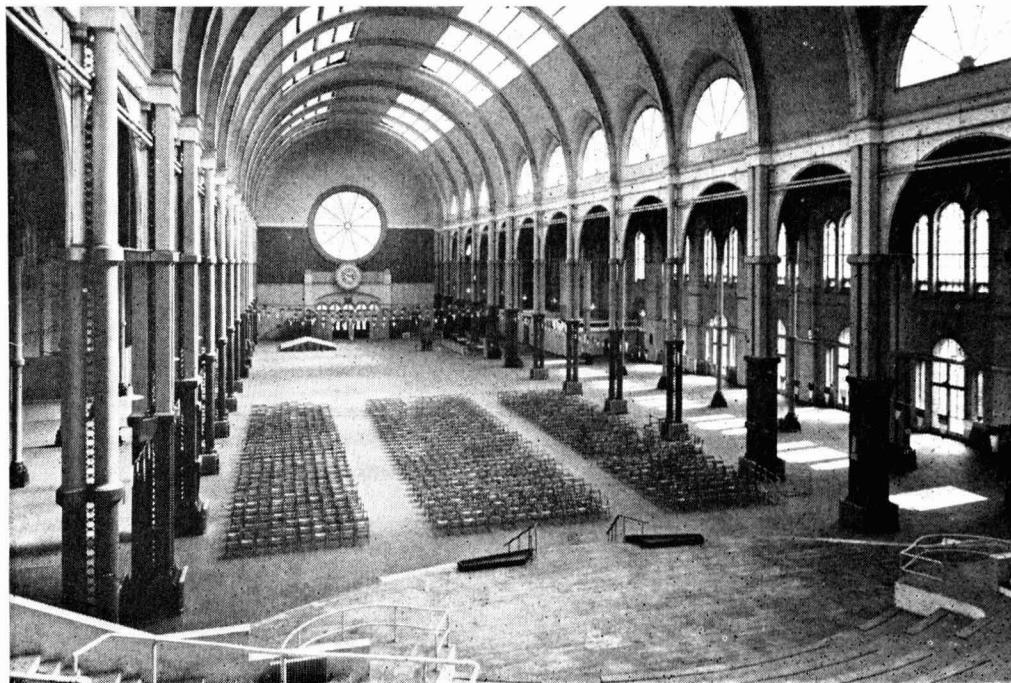


Photo by

Leslie Bryce, A.I.B.P., A.R.P.S.

THE GREAT HALL OF ALEXANDRA PALACE



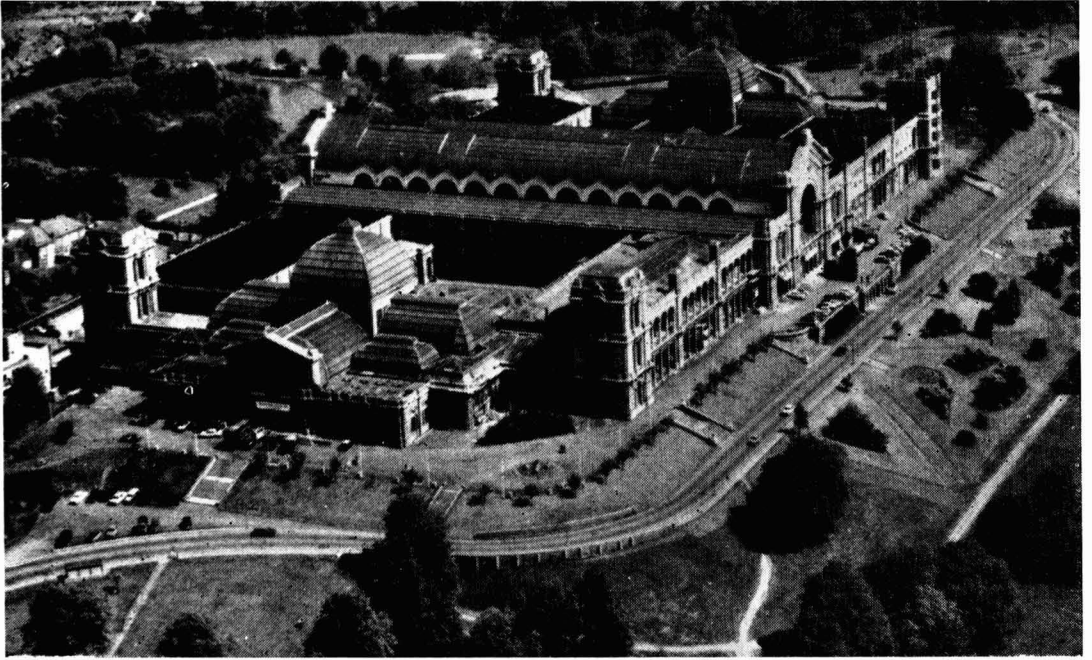


Photo by

*Aerofilms & Aero Pictorial*

AERIAL PHOTOGRAPH OF ALEXANDRA PALACE, SHOWING (IN THE CENTRE) THE GREAT HALL, WHERE THE EXHIBITION WILL BE HELD



Photo by

*Leslie Bryce, A.I.B.P., A.R.P.S.*

A CORNER OF ONE OF THE TWO RESTAURANTS AT ALEXANDRA PALACE

# Section Programmes for 1964-65 Session

## SCOTTISH SECTION

All technical meetings commence at 7.30 p.m.

**1964**

**Thursday 8 October**

"The Selection and Efficient Operation of Shot Blasting Equipment," by Mr. W. R. MacMillan, followed by a film, "The Blast Cleaning of Steel," at the Grand Hotel, Glasgow.

**Thursday 12 November**

"The Development of Water Soluble Resins," by Mr. A. G. North, at More's Hotel, Glasgow.

**Thursday 10 December**

"The Function and Place of the Stock Exchange in Everyday Life," by Mr. O. Speirs, and the film, "My Word Is My Bond," at More's Hotel, Glasgow.

**1965**

**Thursday 14 January**

"A General Review of Driers," by Mr. J. W. H. Turner, at More's Hotel, Glasgow.

**Friday 15 January**

Annual Dinner-Dance at the Central Hotel, Glasgow, at 6.30 p.m.

**Thursday 11 February**

"Zinc Dust and Flake Pigments," by Mr. D. A. Atkinson, at More's Hotel, Glasgow.

**Thursday 11 March**

"Printing and Metal Decoration," by Mr. A. D. Lott, at More's Hotel, Glasgow.

**Friday 9 April**

Annual General Meeting at the St. Enoch Hotel, Glasgow, at 6 p.m., followed by the Annual Smoking Concert at Eglinton Arms Hotel, Eaglesham, at 7.30 p.m.

## SCOTTISH SECTION—STUDENT GROUP

All meetings to be held at More's Hotel, Glasgow, at 10 a.m.

**1964**

**Saturday 12 September**

Film Show.

**Saturday 10 October**

*Tutorials*: 1. Introduction to Paint Technology—Mr. D. M. Stewart. 2. Paint Manufacture—Mr. J. S. Hutchison. 3. Printing Ink—Mr. G. H. Hutchinson.

**Saturday 14 November**

*Tutorials*: 1. Pigments—Mr. P. Birrell. 2. Two-Pot Systems—Mr. J. Miller. 3. Introduction to Plastics—speaker from Shell Chemicals Ltd.

**Saturday 12 December**

Film Show.

**1965**

**Saturday 16 January**

*Tutorials*: 1. Alkyd Resins—Mr. W. Maxwell Young. 2. Emulsion Paints—Mr. A. McLean. 3. Driers—Dr. D. Atherton.

**Saturday 13 February**

Annual General Meeting. Members' Discussion Morning.

**Saturday 13 March**

*Tutorials*: 1. Paint Media Other Than Alkyd Resins—Mr. A. McGuire. 2. Inorganic Pigments—Mr. J. Waters. 3. Speaker from Paint Research Station.

## WEST RIDING SECTION

All meetings will be held at the Great Northern Hotel, Leeds, at 7.30 p.m. unless otherwise stated.

1964

**Tuesday 8 September**

"Staff for the Paint Industry," by Mr. M. H. M. Arnold.

**Tuesday 13 October**

"Crystal Form and Colour Properties of Pigments," by Dr. D. Patterson, of the Department of Colour Chemistry (Leeds University).

**Tuesday 10 November**

"Theory and Practice in the Use of Colour," by Miss R. A. Rathbone.

**Friday 27 November**

Annual Dinner and Dance to be held at the Granby Hotel, Harrogate.

1965

**Tuesday 12 January**

"Furoic Acid in Alkyds," by V. F. Jenkins.

**Thursday 25 February**

Joint Meeting with the Society of Chemical Industry on Pigment Wetting. Introductory paper, "Pigment Dispersion Agents," by Mr. Schwitzer, and "Pigment Dispersion and Pigmentation Structure," by R. J. Cole, of the Paint Research Station.

**Tuesday 9 March**

"Printing On Plastics," by Mr. A. J. G. Shaw.

**Tuesday 13 April**

Annual General Meeting.

CITY AND GUILDS OF LONDON INSTITUTE  
EXAMINATION RESULTS

Congratulations are extended to the following members of the Association upon their success in the recent City and Guilds of London examinations. The class of membership and the Section to which the member is attached are shown in italics.

*Intermediate Examination in Paint Technology*

M. J. Bedford (*Junior-London*), D. T. Catchpole (*Junior-London*), M. B. Hall (*Junior-London*), G. T. Hardy (*Junior-London*), J. E. Judah (*Ordinary-London*), J. W. Kennedy (*Junior-London*), D. E. Steed (*Ordinary-London*), G. Asten (*Ordinary-Manchester*), M. Bell (*Ordinary-Manchester*), G. Blackburn (*Ordinary-Manchester*), G. T. Flood (*Ordinary-Manchester*), M. E. Williams (*Associate-Manchester*), E. Greenfield (*Associate-Midlands*), P. J. H. Watson (*Junior-Newcastle*), D. M. Wren (*Ordinary-Newcastle*).

*Advanced Examination in Paint Technology*

D. H. Deacon (*Associate-London*), B. Evans (*Junior-London*), C. W. Kirlew (*Ordinary-*

*London*), R. K. Pal (*Ordinary-London*), J. Moore (*Associate-Manchester*), B. R. Bell (*Ordinary-Midlands*), A. R. Crump (*Junior-Midlands*), E. S. Millington (*Junior-Midlands*), A. C. Saxby (*Ordinary-London*), D. Lonsdale (*Associate-West Riding*), A. J. Durdey (*Junior-Newcastle*).

*Painting Technology—Full Technological Certificate in Works Organisation*

R. K. Pal (*Ordinary-London*), D. W. Mendez (*Ordinary-London*), G. W. N. Robinson (*Ordinary-London*), D. Andrews (*Ordinary-Manchester*).

*Painting Technology—Full Technological Certificate in Pigment Manufacture*

J. W. Johnstone (*Ordinary-Manchester*).

*Paint Technology—Full Technological Certificate in Application of Surface Coatings*

C. Lever (*Ordinary-Manchester*), F. B. Windsor (*Ordinary-Manchester*).

*Paint Technology—Full Technological Certificate in Polymer Chemistry in Surface Coating Technology*

S. C. Datta (*Ordinary-London*), M. M. Eames (*Ordinary-London*), D. W. Helmsley (*Junior-London*), G. D. Bird (*Ordinary-Midlands*).

## PROGRAMME LIAISON COMMITTEE

The Liaison Committee, comprising two representatives each from the Institution of the Rubber Industry (*IRI*), the Plastics Institute (*PI*), the Plastics and Polymer Group of the Society of Chemical Industry (*SCI*) and *OCCA*, was formed in order to obviate the inconvenience caused by the clashing of dates of symposia, conferences, exhibitions, etc., of the different bodies. Forthcoming major meetings or conferences on polymers or related topics planned by the above societies and others are given below; they will be in London, unless otherwise stated.

**1964**

13 to 15 October

Third International Synthetic Rubber Symposium and Rubber Exhibition.

14 October

Symposium on "Thin Layer Chromatography" at Birmingham University (The Society of Analytical Chemistry).

21 October

Dinner at the Europa Hotel (British Plastics Federation).

19 November

Third Swinburne Award Address (*PI*).

25 to 27 November

Fourth International Reinforced Plastics Conference (British Plastics Federation).

**1965**

1 January

Young People's Lecture (*PI*).

22 to 26 March

Technical Exhibition (*OCCA*).

24 March

Conference on "Research Projects" (*PI*, Reinforced Plastics Group).

22 and 23 April

Symposium on "The Chemistry of Polymerisation Processes" (*SCI*).

25 to 29 May

Technical Conference at Torquay (*OCCA*).

14 to 16 June

Conference on "Plastics in Building Structures" (*PI* in association with the Institution of Structural Engineers, the Royal Institute of British Architects and the Institution of Civil Engineers).

16 to 26 June

Interplas.

22 June

Dinner at the Connaught Rooms (*PI*).

7 to 9 July

Symposium on "Molecular Relaxation Processes" (The Chemical Society).

12 to 17 July

XIIth International Spectroscopy Colloquium at Exeter.

**1966**

March

Conference on "Flame Resistant Polymers" (*PI*).

May

Joint Conference on "Advances in Polymer Science and Technology" (*SCI/IRI/OCCA/PI*).

---

**IUPAC 1965**

The 20th International Congress of Pure and Applied Chemistry will be held in Moscow, USSR, from 12-18 July 1965. The programme will consist of about 20 invited lectures and about 500 contributed papers. Further information can be obtained from the Secretary-General, the Executive Committee of the XXth International Congress of Pure and Applied Chemistry, Institute of Chemical Physics, Academy of Sciences, Vorobyevskoye Chausee 2-b, Moscow V-334, USSR.

---

**BRITISH STANDARDS**

Three new British Standards, prepared under the committee on which the Association is represented, have just been issued. They are :

BS 3599/6-15 : 1964 : Organic pigments for paint.

BS 3773 : 1964 : Phthalic anhydride.

BS 3774 : 1964 : Maleic anhydride.

Copies of these Standards can be obtained from the British Standards Institution (Sales Branch), 2 Park Street, London, W.1, at the following prices : BS 3599, 17s. 6d. ; BS 3773 and BS 3774, 6s.

#### 1965 MEMBERS' SUBSCRIPTIONS

Members may like to be reminded that 1965 Membership Subscriptions to the Association are payable on 1 January 1965. Forms have already been despatched to those in the General Overseas Section and will be despatched to those in the United Kingdom Section and Branches in November.

New members may like to know that the Commissioners of Inland Revenue had approved of the Association for the purpose of the Finance Act, 1958, Section 16, so that a member subject to United Kingdom income tax is entitled to a deduction from the amount of his emoluments assessable to income tax under Schedule E for the whole of his annual subscription to the Association, provided the subscription is defrayed out of the emoluments of his office or employment and that the interests covered by the

objects of the Association are relevant to such office or employment.

Claims for adjustment of PAYE code numbers should be made on form P.358, copies of which may be obtained from local tax offices.

#### —————

#### DIAZOTISATION AND DIAZO COMPOUNDS

A one-day symposium on the subject of "Diazotisation and Diazo Compounds" will be held on 31 October 1964 at the Leicester College of Technology. The symposium will consist of two sessions, two papers being read at each. Anyone wishing further details should write to the Registrar, Leicester College of Technology, Leicester.

#### —————

#### NEWS OF MEMBERS

Mr. R. J. McCausland, an Ordinary Member attached to the London Section, has been appointed technical director of Jensen and Nicholson Ltd., with responsibility for the control of the development of industrial and decorative paints.

Mr. P. Walker, an Ordinary Member attached to the London Section and Honorary Treasurer of the Thames Valley Branch, has been awarded the City and Guild Insignia Award following the submission of a thesis on "The Chemistry and Technology of Surface Coatings Based on Polyisocyanates."

## Obituary

### MR. A. L. BROWN

It was a great shock to many in the industry to hear of the death of Mr. Alan Lee Brown.

Alan was an Associate of the Royal Australian Chemical Institute and was a member of the New South Wales Section of OCCA. He joined the Association soon after the first Australian Section was formed and was an active member for many years.

In his 32 years with Lewis Berger & Sons he rendered valuable service in both the

research and industrial sales fields, and it was only early this year that he was appointed technical manager of the Australian company after having been manager of the industrial division for the previous six years.

His untimely death has been a great loss not only to his family and friends but to his company and the paint industry as a whole.

Our sincere sympathy is extended to Mrs. Brown and the two children.

M. LEAHEY.

## 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

- BARNHILL, STANLEY ROBERT BOOTH, A.S.T.C., B.S.C., Flat 2, 2 Cadia Street, Kogarah, New South Wales, Australia. (*New South Wales*)
- BRAY, JOHN CHARLES, 119 Railway Street, Altona, Victoria, Australia. (*Victorian*)
- BRIDGETT, GRAEME ERIK, c/o Henry H. York & Co. Pty. Ltd., 376-394 Whitehorse Road, Nunawading, Victoria, Australia. (*Victorian*)
- BUNN, GEOFFREY CHARLES, Red Tiles, Victoria Road, Clifton, Cape Town, South Africa. (*South African*)
- DAVISON, ROBERT LESLIE, c/o British Paints (WA) Ltd., PMB 1052, Ikeja, Western Region, Nigeria. (*Overseas*)
- ELLIS, RUSSELL GEORGE, "Illangi," Bradley's Lane, Warrandyke, Victoria, Australia. (*Victorian*)
- FREEMAN, JOHN RICHARD, B.S.C., 12 Argyle Avenue, Ryde, New South Wales, Australia. (*New South Wales*)
- HEATH, NEIL STEWART, M.S.C., PH.D., 2 Victoria Street, Upper Fern Tree Gully, Victoria, Australia. (*Victorian*)
- HOBBY, RUSSELL KEITH, A.R.A.C.I., Leonard Chemical Products Pty. Ltd., Edward Street, East Oakleigh, Victoria, Australia. (*Victorian*)
- HOWELLS, MAXWELL, Lot 133, Fearn Street, Toongabbie, 1W, New South Wales, Australia. (*New South Wales*)
- KOCZKAR, GEORGE MICHAEL, B.S.C., A.S.T.C., 19 Churchill Crescent, Cammeray, New South Wales, Australia. (*New South Wales*)
- MURFIN, TREVOR MORTON, Killrust Pty. Ltd., Railway Parade, Rocklea, Brisbane, Queensland, Australia. (*Queensland*)
- NOORDWEIER, HANS, B.S.C., Flat 5, 37 Sir Thomas Mitchell Road, Bondi, New South Wales, Australia. (*New South Wales*)
- OWEN, WILLIAM JOHN, F.R.I.C., Chemitrade Ltd., Berkeley Square House, Berkeley Square, London, W.1. (*London*)
- PINNINGTON, AUSTIN ROBINETTE, M.A., D.PHIL., Laporte Titanium Ltd., New Bond Street, London, W.1. (*London*)
- ROGERS, CECIL JOHN, 8 North Street, Auburn, New South Wales, Australia. (*New South Wales*)
- SHEAFFE, BRIAN LEMPRIERE, B.S.C., 1A Telfer Road, Castle Hill, New South Wales, Australia. (*New South Wales*)
- SPARGO, ALBERT BASIL, 32 Groote Schuur, 2 Erskine Terrace, South Beach, Durban, South Africa. (*South African*)
- TUFAIL, MOHAMMAD, M.S.C., PH.D., 9 Firoze Street, Garhi Shahu, Lahore, West Pakistan. (*Overseas*)
- VAN NIMWEGAN, JACOB, Point Pleasant, Durbanville Avenue, Durbanville, Cape, South Africa. (*South African*)
- WALMSLEY, JOHN, 27 Marriott Road, Durban, Natal, South Africa. (*South African*)
- WRIGHT, GRAHAM JAMES, A.S.T.C., Defence Standards Laboratories, Box 60 PO, Alexandria, New South Wales, Australia. (*New South Wales*)



### Associate Members

- COMERY, DOUGLAS ARTHUR, 30 McPherson Street, Moonee Ponds, Victoria, Australia.  
(Victorian)
- EDWARDS, THOMAS EDWARD, 3 Botany Street, Randwick, Sydney, New South Wales,  
Australia. (New South Wales)
- FUCHS, ERNST GÜNTER, 27 Ben Roma, Ocean View Drive, Sea Point, Cape Town,  
South Africa. (South African)
- GOLDSWORTHY, LEONARD MICHAEL, S. W. Church & Co. Pty. Ltd., 328 Flinders Street,  
Melbourne, Victoria, Australia. (Victorian)
- JANSEN, HERMANN-JOSEF, Hoechst SA (Pty.) Ltd., PO Box 4846, Cape Town, South  
Africa. (South African)
- MACCARTHY-MORROGH, BRIAN JAMES, 106 Pupuke Road, Birkenhead, Auckland, New  
Zealand. (Auckland)
- MUSGRAVE, KEVIN, PH.C., 289 Roberts Road, Greenacre, New South Wales, Australia.  
(New South Wales)
- SELL, DOUGLAS WINSTON, 7 Romford Road, Papatoetoe, Auckland, New Zealand.  
(Auckland)
- SMART, FRANCIS AUSTIN, Unilever (Aust.) Pty. Ltd., 164 Ingles Street, Port Melbourne,  
Victoria, Australia. (Victorian)
- VALENTINE, WILLIAM JAMES MURRAY, c/o Union Carbide NZ Pty. Ltd., PO Box 14108,  
Panmure, Auckland, E.2, New Zealand. (Auckland)
- WAGNER, WOLFGANG J., c/o H. H. York & Co. Pty. Ltd., Box 3957, GPO, Sydney,  
New South Wales, Australia. (New South Wales)

### Junior Members

- AYTON, ROBERT THOMAS, 145 Sunshine Road, Tottenham, W.12, Victoria, Australia.  
(Victorian)
- CHANDLER, BARRY LESLIE, 13 Salisbury Street, Newport, W.15, Victoria, Australia.  
(Victorian)
- DAPIRAN, GIANPIETRO, 23 Ballard Street, Yarraville, W.13, Victoria, Australia.  
(Victorian)
- TRETHOWAN, WILLIAM FRANCIS, Keilor Road, Rockbank, Victoria, Australia.  
(Victorian)

## 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 after publication.)

### Thursday 1 October

*Midlands Section—Trent Valley Branch.* "Current Developments in Dispersion," by G. Cope, at British Railways School of Transport Lecture Theatre, at 7.30 p.m.

*Newcastle Section.* "Paint and the Consumer," by J. Dukes (*Which?*), at the Crown Hotel, Newcastle, at 6.30 p.m.

### Wednesday 7 October

Council meeting at 2 p.m. and Past Presidents' Dinner at 6.30 p.m. for 7 p.m.

### Thursday 8 October

*Scottish Section.* "The Selection and Efficient Operation of Shot-Blasting Equipment," by W. R. MacMillan. Film: "The Blast Cleaning of Steel." at the Grand Hotel, Glasgow, at 7.30 p.m.

### Friday 9 October

*Hull Section.* Annual Dinner-Dance at the New York Hotel, at 7 p.m.

*Manchester Section.* "The Electro-deposition of Paint," by A. G. North, at the Strand Hotel, Liverpool, at 6.30 p.m.



**Saturday 10 October**

*Scottish Section—Student Group.* Tutorials: (1) "Introduction to Paint Technology," by D. M. Stewart, (2) "Paint Manufacture," by J. S. Hutchison, (3) "Printing Ink," by G. H. Hutchinson, at More's Hotel, Glasgow, at 10 a.m.

**Monday 12 October**

*London Section—Southern Branch.* "Pigmentation of Finishes for Electrodeposition," by J. R. Taylor, at the Royal Hotel, Cumberland Place, Southampton, at 7.30 p.m.

**Tuesday 13 October**

*West Riding Section.* "Crystal form and Colour Properties of Pigments" by Dr. D. Patterson at the Great Northern Hotel, Leeds, at 7.30 p.m.

**Wednesday 14 October**

*Scottish Section—Eastern Branch.* "Work Study," by J. Gloag (Heriot Watt College), at the North British Hotel, Edinburgh, at 7.30 p.m.

**Thursday 15 October**

*London Section—Thames Valley Branch.* "Objective Approaches to Colour Matching and Production Control," by J. L. R. Landry, at the Royal White Hart, Beaconsfield, at 7 p.m. Refreshments at 6.30 p.m.

*Midlands Section.* Day Symposium—"Electrodeposition of Paint," at Regency Club, Shirley, at 10.30 a.m.

*Queensland Section.* Wine Tasting Evening.

**Saturday 17 October**

*Auckland Section.* Ladies' Night at Flamingo Cabaret (17 or 24 October).

**Wednesday 21 October**

*Auckland Section.* General Meeting. Speaker: Mr. Brooker (21 or 28 October).

**Thursday 22 October**

*London Section.* "Inherent Properties of Paint Latex Films in Relation to their Performance," by H. Oosterhof, at the Royal Society of Tropical Medicine and Hygiene, Manson House, 26 Portland Place, London, W.1, at 7 p.m.

*Wellington Section.* "Raw Materials for the Paint Trade from New Zealand Sources" by D. S. Nicholson.

**Friday 23 October**

*Manchester Section.* Annual Dinner and Dance, at the Midland Hotel, Manchester.

**Friday 30 October**

*Bristol Section.* "Printability of Paper and Board," by Miss E. J. Pritchard (PATRA), at the Royal Hotel, College Green, Bristol, at 7.15 p.m.

*Bristol Section—Irish Branch.* "Modern Plant and Materials for Finishing and Painting Automobiles," by J. Walker, at the Dolphin Hotel, Essex Street, Dublin, at 8 p.m.

**November**

*Wellington Section.* Ladies' Night (date to be advised).

**Monday 2 November**

*Hull Section.* Joint Meeting with the Hull NFMP, at the Royal Station Hotel, Hull, at 7.15 p.m.

**Monday 9 November**

*London Section—Southern Branch.* "Durability Testing of Titanium Oxide Pigments," by E. Oakley, at the Queens Hotel, Southsea, at 7.30 p.m.

**Tuesday 10 November**

*West Riding Section.* "Theory and Practice in the Use of Colour" by Miss R. A. Rathbone, at the Great Northern Hotel, Leeds, at 7.30 p.m.

**Wednesday 11 November**

*Scottish Section—Eastern Branch.* “Paper/Printing Inks Relationships,” by A. T. Franklin, at the North British Hotel, Princes Street, Edinburgh, at 7.30 p.m.

**Thursday 12 November**

*London Section.* “Mould Resistance of Paints in the Tropics,” by P. Whiteley (Building Research Station), at The Royal Society of Tropical Medicine and Hygiene, Manson House, Portland Place, London, W.1. at 7 p.m.

*Midlands Section—Trent Valley Branch.* “Colour Consciousness,” by Dr. F. M. Smith, at British Railways School of Transport Lecture Theatre, at 7.30 p.m.

*Newcastle Section.* “Industrial Finishes in the Appliance Field,” by Dr. H. S. Sharp, at 6.30 p.m.

*Scottish Section.* “The Development of Water Soluble Resins,” by A. G. North, at More’s Hotel, Glasgow, at 7.30 p.m.

**Saturday 14 November**

*Scottish Section—Student Group.* Tutorials : (1) “Pigments,” by P. Birrell, (2) “Two-Pot Systems,” by J. Miller, (3) “Introduction to Plastics,” by speaker from Shell Chemicals Ltd., at More’s Hotel, Glasgow, at 10 a.m.

**Tuesday 17 November**

*Hull Section.* Discussion Evening at the Queen’s Hotel, at 7.15 p.m.

*London Section—Thames Valley Branch.* “Antimony Oxide in Flame Retardant Paints,” by A. G. Walker, at Royal White Hart, Beaconsfield, at 7 p.m. Refreshments at 6.30 p.m.

**Thursday 19 November**

*Queensland Section.* “Recent Developments in Polymethane Raw Materials,” by J. Samios.

**Friday 20 November**

OCCA Council Meeting (morning).

*London Section.* Ladies’ Night, at 7 p.m.

*Midlands Section.* “What Is Pigment Dispersion?”, by Dr. F. M. Smith, at Birmingham Chamber of Commerce, Edgbaston, at 6.30 p.m.

*Manchester Section.* “Dispersion Stabilisation Mechanisms In Paint Systems,” by W. Black, at Manchester Literary and Philosophical Society, George Street, Manchester, at 6.30 p.m.

**Friday 27 November**

*Bristol Section.* “Painting of Plasters” —Film Show and Discussion. Joint Meeting with Birmingham PVL Club, at Hawthorn Hotel, Bristol, at 6.30 p.m.

*Bristol Section—Irish Branch.* “Native Irish Timber,” by T. Ferguson (Irish Institute for Industrial Research and Standards), at the Dolphin Hotel, Essex Street, Dublin, at 8 p.m.

*South Australian Section.* Annual Dinner at the Buckingham Arms Hotel, Gilberton.

**Saturday 28 November**

*Wellington Section.* “Ladies’ Night” (details to be advised).

**Thursday 17 December**

*Queensland Section.* Annual Christmas Party.

## Oil and Colour Chemists' Association

*President* : J. E. ARNOLD, B.SC., PH.D., F.R.I.C., A.INST.P.

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 used in their manufacture. In 1923 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 (with an Irish Branch), Hull, London (with Southern and Thames Valley Branches), Manchester, the Midlands (with a Trent Valley Branch), Newcastle upon Tyne, New South Wales, Queensland, Scotland (with an Eastern Branch), South Africa (with Branches in the Cape, Transvaal and Natal), South Australia, Victoria, Wellington, West Australia 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).

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Junior 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 three guineas, except for Junior Members whose subscription is 10s. 6d. 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 General 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, £5 p.a. post free ; abroad, £6 p.a. post free ; payable in advance.  
*An Introduction to Paint Technology* (Second Edition). Pp. 187, illustrated, with index, 15s. (including postage).

### *Paint Technology Manuals*

- Part 1 : " Non-convertible Coatings," Pp. 326, 35s.
- Part 2 : " Solvents, Oils, Resins and Driers," Pp. 239, 35s.
- Part 3 : " Convertible Coatings," Pp. 318, 35s.

General Secretary : R. H. Hamblin, M.A., F.C.I.S., F.C.C.S., Wax Chandlers' Hall, Gresham Street, London, E.C.2.

POLAR WHITENESS

TROPICAL BRIGHTNESS



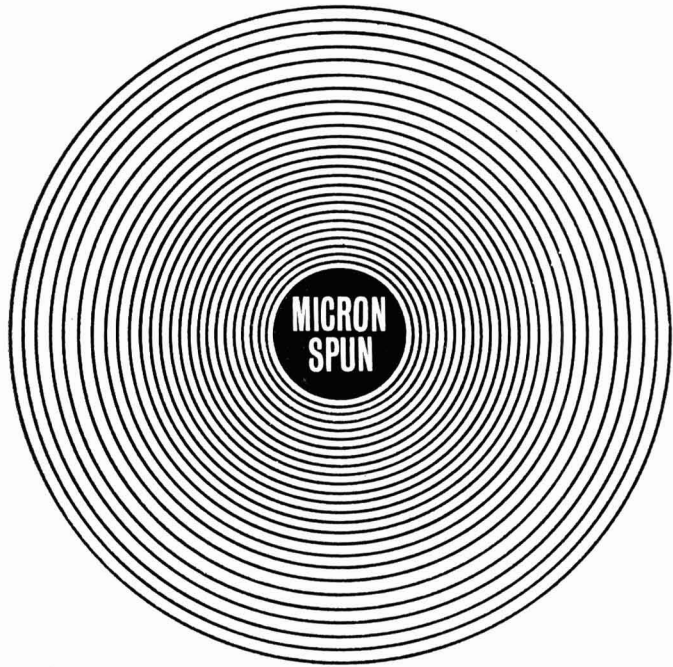
**LAPORTE**

**TITANIUM OXIDE**



LAPORTE TITANIUM LIMITED · NEW BOND STREET HOUSE · LONDON · W.1  
*A member of the Laporte Industries Group*

HAT.15



## What's in a name?



Just as the Greek letter  $\mu$  means ONE MILLIONTH OF A METRE (i.e. 1 MICRON) so the name MICRONSPUN is your assurance of a pigment manufactured to unequalled Micron fineness. MICRONSPUN is the new registered name for G.V. Micronized Pigments; it signifies products proven in use and backed by 16 years of G.V. micronizing experience. You can be confident that their quality and fineness will be reflected in your output.

# MICRONSPUN

THE REGISTERED NAME OF

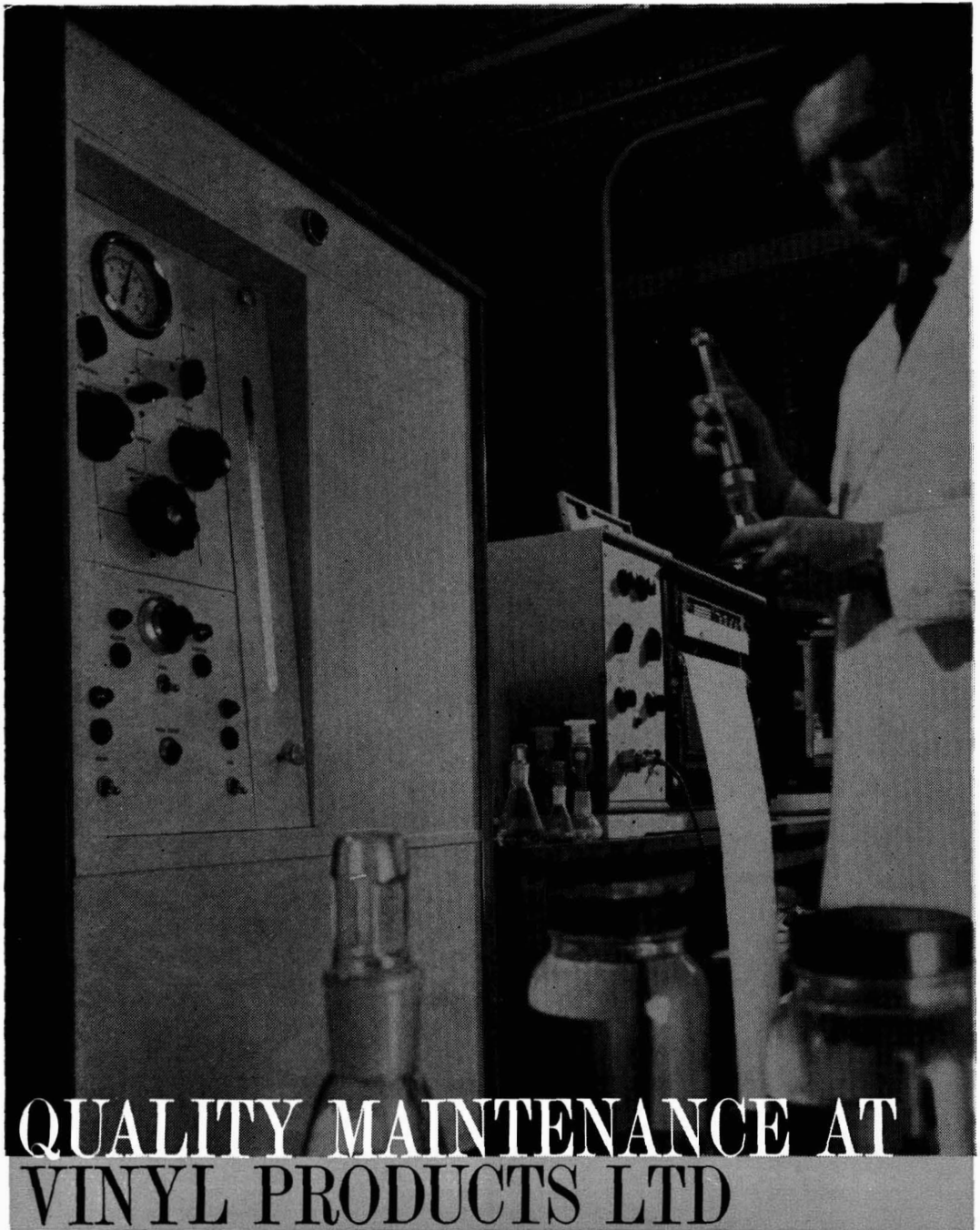
## MICRONIZED PIGMENTS

MICRON SPUN PRODUCTS INCLUDE:  $\mu$  PRIMER OXIDES ·  $\mu$  RED OXIDES  
 $\mu$  OCHRE ·  $\mu$  EXTENDERS ·  $\mu$  PRUSSIAN BLUE ·  $\mu$  BROWN ·  $\mu$  GREENS

For easy dispersion in paint, plastics.

Write for literature on individual pigments  
 in the G.V. range.

**GOLDEN VALLEY COLOURS LTD., WICK, BRISTOL**



# QUALITY MAINTENANCE AT VINYL PRODUCTS LTD

Rigid laboratory control, employing the most modern methods and equipment, guarantees the batch-to-batch uniformity which has given Vinamu!, Vinacryl, Vinalak and Vinapol synthetic resin emulsions and solutions their world-wide reputation for consistently high quality.



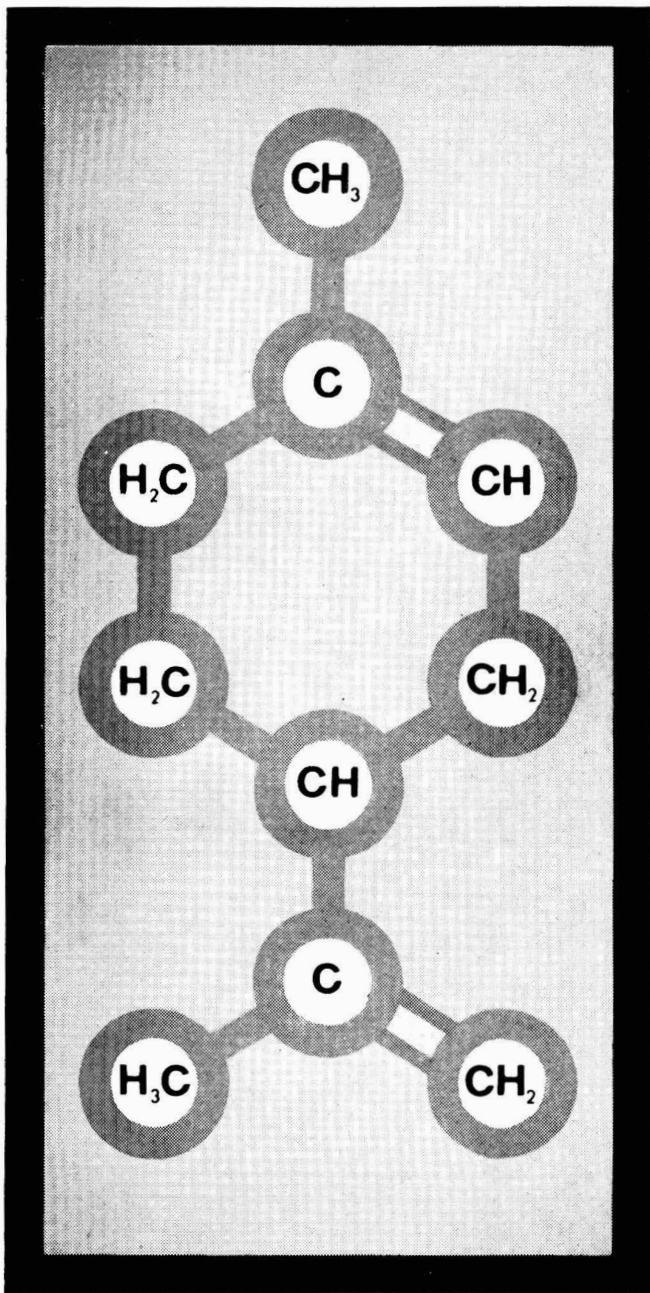
**VINYL PRODUCTS LTD • CARSHALTON SURREY • VIGilant 6044**

A member of the Reichhold Chemicals Ltd. Group

VP.108A



# BXP Dipentene



for paints, varnishes, essential oils, cleaners, polishes, lubricants, perfumery, rubber compounds, paracymene and paramenthane preparations and cyclohexane derivatives.

BXP dipentene is neutral, free from visible water, suspended matter and corrosive sulphur compounds, and has a pleasant lemon-like smell. It conforms to British Standard 2712 specifications and can be hydrogenated, dehydrogenated, oxidized and polymerised. It reacts with formaldehyde, halogens, hydrogen sulphide, maleic anhydride and sulphur, yielding important derivatives, for instance terephthalic acid, used for synthetic fibres, or cyclohexane derivatives like the plasticiser dicyclohexyl phthalate. Send for full specifications and applicational fields of this versatile material.

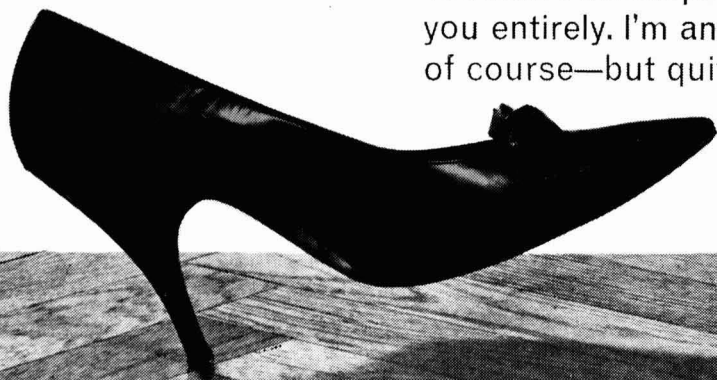
**BXP**

**BX PLASTICS LTD**

*A Bakelite Xylonite Company*  
Manningtree Essex  
Manningtree 2401



"A wood block floor! Mmm. I shall enjoy picking holes in you. Wouldn't be surprised if I didn't ruin you entirely. I'm an absolute heel of course—but quite irresistible"



"Oh yes? Then I've got news for you. I'm finished with Beckurane. A whole army of you—and you still wouldn't make the slightest impression on me"

BECKURANES 2-253, 2-249, M-121, M-180, M-186, Two-Pack and moisture curing Beckuranes can be supplied to give a variety of coatings which may be used for high grade decorative use, flooring finishes and generally in applications where hard wearing qualities coupled with chemical inertness, are required.

**BK**



BECK, KOLLER & CO. (England) LTD., Speke, Liverpool, 24, Tel.: HUNts Cross 1214. Associate Works : Reichold Chemicals Inc., Detroit, U.S.A. Sole Selling Agents : JAMES BEADEL & CO. LTD., Frodsham House, Edwards Lane, Liverpool, 24. Tel: HUNts Cross 1395. London Office, Hillgate House, 26 Old Bailey, E.C.4. Tel. and Grams.: CITY 2405/7. Members of the Reichold Chemicals Ltd. Group of Companies.

# **REGOLITE Paint Pigments**

For outstanding value:

**REGOLITE FAST RED RLS**

(Toluidine Red)

**REGOLITE FAST YELLOW G and 10 G**

(Arylamide Yellows)

And for quality and value examine our:

**REGOLITE AQ STAINERS**

(Aqueous dispersions)

**REGOLITE MT TINTERS**

(Multi-tint dispersions)

Samples and literature are available on request



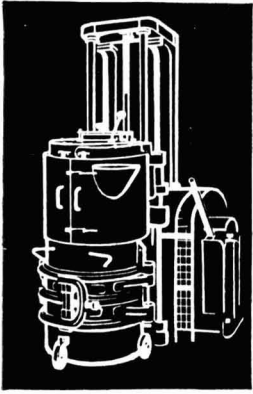
**Resinous Chemicals Limited**

BLAYDON CO. DURHAM. TELEPHONE: BLAYDON 2751

London Office: 32 Sloane Street London S.W.1.

Telephone: BELgravia 3234

SPECIALISTS IN RESINS, PIGMENTS AND PLASTICS



## Good paint in the making...

**KEENOMIX** This heavy duty paste mixer is widely used in the paint and ink industries where the advantages of efficient pre-mixing of materials prior to milling are being increasingly recognised. The action of the Keenomix assures a high degree of dispersion of pigments in media before milling. Milling rates are increased and mill maintenance costs reduced; in some instances the milling operation may even be entirely eliminated. The geared rotary mixing head and blades are lifted and lowered hydraulically. A descriptive leaflet is available on request.

### VICKERS-BUILT FOR RELIABILITY AND LONG LIFE

The Vickers Keenomix is just one of a range of modern paint-producing machines engineered by Vickers—for milling, refining and mixing of paints, inks and similar products. Equipments like this are helping the modern paint industry to achieve high output of fine quality products, and have proved their reliability and efficiency in active service — the most vital test of all!

# VICKERS

**INTRODUCTION TO****paint****TECHNOLOGY****SECOND EDITION NOW AVAILABLE**

Revised by A. A. Drummond, M.Sc., A.R.I.C., under the Editorship of I. C. R. Bews, B.Sc., A.R.I.C., in consultation with T. E. Johnson, A.M.C.T., F.R.I.C.

---

Because of the enormous success of the first edition (10,000 copies sold) and the rapid advances made in the technology of the Paint and Allied Industries during the past decade, the Council of the Oil and Colour Chemists' Association has authorised the complete revision of the "Introduction to Paint Technology."

The second edition will prove (as did the first edition) of immense value not only to young entrants into the industries but also to technical representatives and others desiring a basic knowledge of the principles and techniques of the Paint and Allied Industries.

---

**LIST OF CONTENTS****ORIGINS AND DEVELOPMENT****OILS****NATURAL AND SYNTHETIC RESINS****OLEORESINOUS ALKYD AND CELLULOSE MEDIA****PIGMENTS****DECORATIVE PAINTS****INDUSTRIAL FINISHES AND TECHNIQUES****PAINT MANUFACTURE AND HAZARDS****PAINT TESTING****COMMON DEFECTS**


---

The book contains 186 pages including 10 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 15s. (post free).



## A FINISHED FLAT LACQUER IN MINUTES!

**Gasil Brand Micronised Silica Gels** and a high speed disperser enable you to prepare a finished flat lacquer in **minutes**.

GASIL 644 and 937 need no ball milling—they augment your plant capacity, and they save time, labour and trouble on an impressive cost-cutting scale because they can be so easily, quickly incorporated into surface coating formulations.

In lacquers and varnishes, the particle sizes of GASIL 644 and 937 make possible an exceptionally accurate control over the degree of mattness required.

*GASIL 644 and 937 are two of a series of fine silicas of carefully controlled properties produced by Crosfield. Each Gasil has been specifically produced for industrial applications, and each one embodies the years of research and manufacture which Crosfield have applied to the field of silicate chemistry*

**FOR FULL DETAILS of Gasil 644 & 937, complete and post this coupon TODAY!**

Name.....

Company address.....

.....

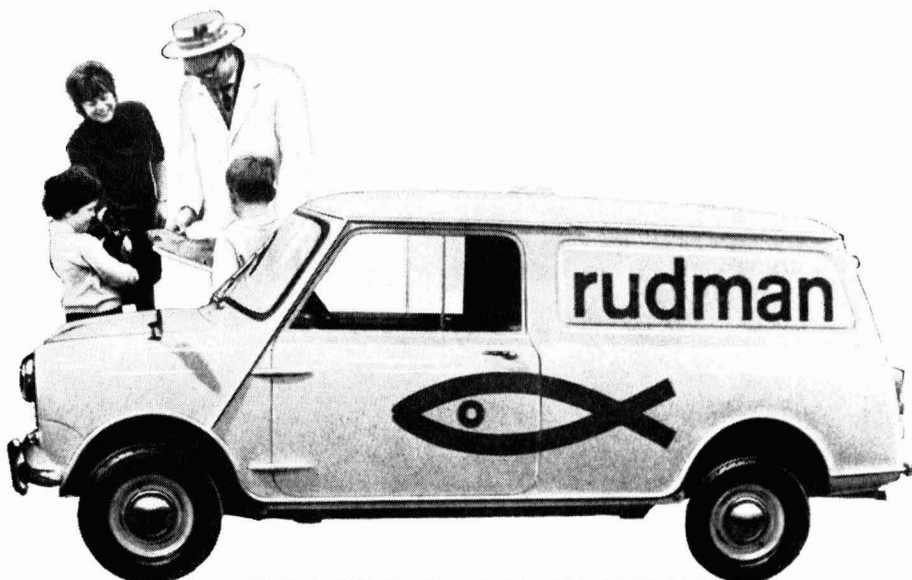
.....

D

GASIL is a registered trade mark



**Joseph Crosfield & Sons Limited**  
**Warrington · Lancashire · Tel: Warrington 31211**



## MINI-VAN AT WORK

This handsome business ambassador and jack of all trades owes much to its acrylic finish—a formulation based on 'Oxitol' acetate.

The exceptional properties of acrylic resins for automobile finishes and refinish lacquers, particularly with respect to their high rate of solvent release, require solvent systems featuring 'Oxitol' acetate as a prime constituent. This high power solvent in the Shell Chemical range is an excellent vehicle for acrylic and other synthetic resins, and along with Shell's ketones, alcohols, glycol ethers and aromatic hydrocarbons, is helping to get the best out of modern coatings.

*Write for technical literature on 'Oxitol' acetate and other Shell chemical solvents.*

## OXITOL ACETATE FOR ACRYLIC FINISHES

Shell Chemicals



**SHELL CHEMICAL COMPANY LIMITED**

Shell Centre, Downstream Building, London S.E.1.

Regional offices: London, Birmingham, Manchester, Glasgow, Belfast and Dublin.

SHELL and OXITOL are trade marks

**surest basis for**  
**GOOD PAINTS\***  
**DUNLOP**  
**POLIMUL**

100% ACRYLIC / ACRYLIC COPOLYMER / ACRYLIC TERPOLYMER  
STYRENE-ACRYLIC / STYRENE-BUTADIENE / PVA HOMOPOLYMER  
IN A RANGE OF GRADES FOR ALL APPLICATIONS

**DUNLOP  
POLYMERS**

\*and Adhesives, Polishes, Sealers & Binders, of course.

*For Technical Information Sheets write to:*



DUNLOP CHEMICAL PRODUCTS DIVISION, CHESTER ROAD FACTORY, BIRMINGHAM, 24.



# MOONSHINE?



CERTAINLY NOT —

PRODUCTS THAT USE HOECHST WAX NEVER WANE

BACKED BY 100 YEARS IN CHEMISTRY

**HOECHST CHEMICALS LIMITED**

Portland House, Stag Place, London, S.W.1. Victoria 2366  
and at Manchester · Birmingham · Leeds · Glasgow



REGISTERED TRADE MARK  
REGISTERED USERS



## A brighter lighthouse with Desmodur/Desmophen.

® Registered Trade Mark

Not only is this lighthouse bright — it is weather resistant and light fast as well! Durable protection against the elements is ensured by the polyurethane surface coating based on Desmodur N/Desmophen 650.

Coatings based on this DD system combine attractive appearance with outstanding adhesion, permanent flexibility and abrasion resistance, first class weather resistance, and above all, absolute light fastness.

If you do not have a lighthouse, the merits of DD coatings have been extensively proved on tramcars, road vehicles and rolling stock, boat hulls and superstructures, cladding — even on such difficult substances as light metals and plastics. — Finishes based on Desmodur N/Desmophen 650 present no health hazard and are applied like any other solvent-based coating. — Write for additional information about Desmodur N and Desmophen 650.

**desmodur/®desmophen**

3068



## J.M. STEEL & CO. LTD.

HEAD OFFICE: KERN HOUSE, 36/8, KINGSWAY, LONDON, W.C.2.

TELEPHONE: HOLBORN 25 32/3/4/5

TELEGRAMS: (INLAND) — COALTAR, WESTCENT, LONDON  
(FOREIGN) — COALTAR, LONDON, W.C.2.

TELEX: LONDON 2 26 40

Kingsway House, 18/24 Paradise Road,  
Richmond, Surrey.

Telephone: Richmond 6077

73/78 King Street, Manchester 2.

Telephone: Deansgate 6077/9

45 Newhall Street, Birmingham 3.

Telephone: Central 6342/3

144 St. Vincent Street, Glasgow C.2.

Telephone: Central 3262/3



Speciality Resins  
for  
all requirements



W. A. MITCHELL & SMITH LTD.  
MITCHAM, SURREY  
Telephone: MITcham 4684-7

# LONABARC

LIMITED

*If you are critical of quality*

*You should be interested in our*

**ALUMINA HYDRATE 5050**

*Sample and details on request*

*Sales Office:* CRANBROOK ROAD, ILFORD, ESSEX.

*Phone:* VALentine 6461/2      *Grams:* Lonabarc Easphone London.



# PRINT IN PRACTICE

Whether you want a letter  
heading or a three-hundred-  
page book—  
printed in one colour or four—  
on newsprint or art paper—  
you will want the best results.

Our services are available  
for consultation on any matter  
of print.

## METCHIM & SON LTD

8 STOREY'S GATE, WESTMINSTER, SW1

Whitehall 7292

## SITUATIONS VACANT



### INGENIEUR CHIMISTE SPECIALISE EN PEINTURES

La PJA est un éminent groupe international fabriquant une vaste gamme de peintures et vernis. Les projets pour sa filiale du Havre, France prévoient de développer la production avec de nouvelles fabrications et permettre une expansion considérable d'ici cinq ans.

L'Ingénieur Chimiste, sous les ordres du Directeur Général de la Société Celomer, aura la responsabilité d'introduire des techniques de laboratoire et des procédés chimiques modernes, et aussi de rationaliser les formules des produits tant industriels que décoratifs. Il travaillera en étroite collaboration avec les services de production et de vente.

*Les conditions requises sont :*

**Age :** 35-45 ans.

**Hiveau :** Diplôme scientifique universitaire ou équivalent.

**Expérience pratique :** Grande expérience de la peinture. Connaissance des problèmes d'application dans l'industrie.

**Qualités requises :** Diplomatie et force persuasive. Capacité d'organisation. Dynamisme.

**Qualités désirables :** De bonnes connaissances de la langue française.

Ce poste s'annonçant difficile au début, il demandera un homme avec le ferme désir de réussir et la tenacité nécessaire pour atteindre le but. C'est une carrière très vaste. Une très bonne rémunération est envisagée dès le début et les perspectives d'avenir sont excellentes.

*S'adresser à :*

**The Managing Director,  
PINCHIN JOHNSON AND ASSOCIATES  
LIMITED**

**Henrietta House, 9 Henrietta Place,  
London, W.1.**

*Toute demande recevra une réponse.*

## CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of 7s. 6d. per line. Advertisements for Situations Wanted are charged at 2s. 6d. per line. A box number is charged at 1s. 0d. They should be sent to the General Secretary, Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2. Telephone: Monarch 1439

### SITUATIONS VACANT

# REVERTEX LIMITED

invite applications for positions in  
the **PAINT LABORATORIES**

● **SENIOR CHEMIST** to lead and expand a team studying new developments in water-thinnable paints. Applicants should be graduates with a very thorough knowledge of paint technology. This is an excellent opportunity for a capable and energetic man with the right background.

● **TECHNOLOGISTS** with appropriate qualifications and experience in the formulation and application of surface coatings.

Salaries for these positions will be negotiable with full recognition of qualifications and experience, and will be supplemented by profit-sharing bonus and other benefits. Applications should be made to :

**LABORATORY MANAGER · REVERTEX LTD · TEMPLE FIELDS · HARLOW · ESSEX**

### BROLAC PAINTS

We invite enquiries from experienced men, under 35 years of age, who are interested in the following technical appointments in our Paint Divisions in Bristol.

1. Development Chemist, Industrial Stoving and Airdrying Products Laboratory.
2. Development Chemist, Water Thinned Decorative Paints Laboratory.
3. Technical Service Chemist, Industrial Sales Division.

These are permanent and progressive appointments, with Pension Scheme and three weeks' Annual Holiday, in an expanding Company.

Write in confidence to The Personnel Officer, John Hall & Sons (Bristol & London) Ltd., PO Box 20, Romilly House, Petherton Road, Bristol, 4.

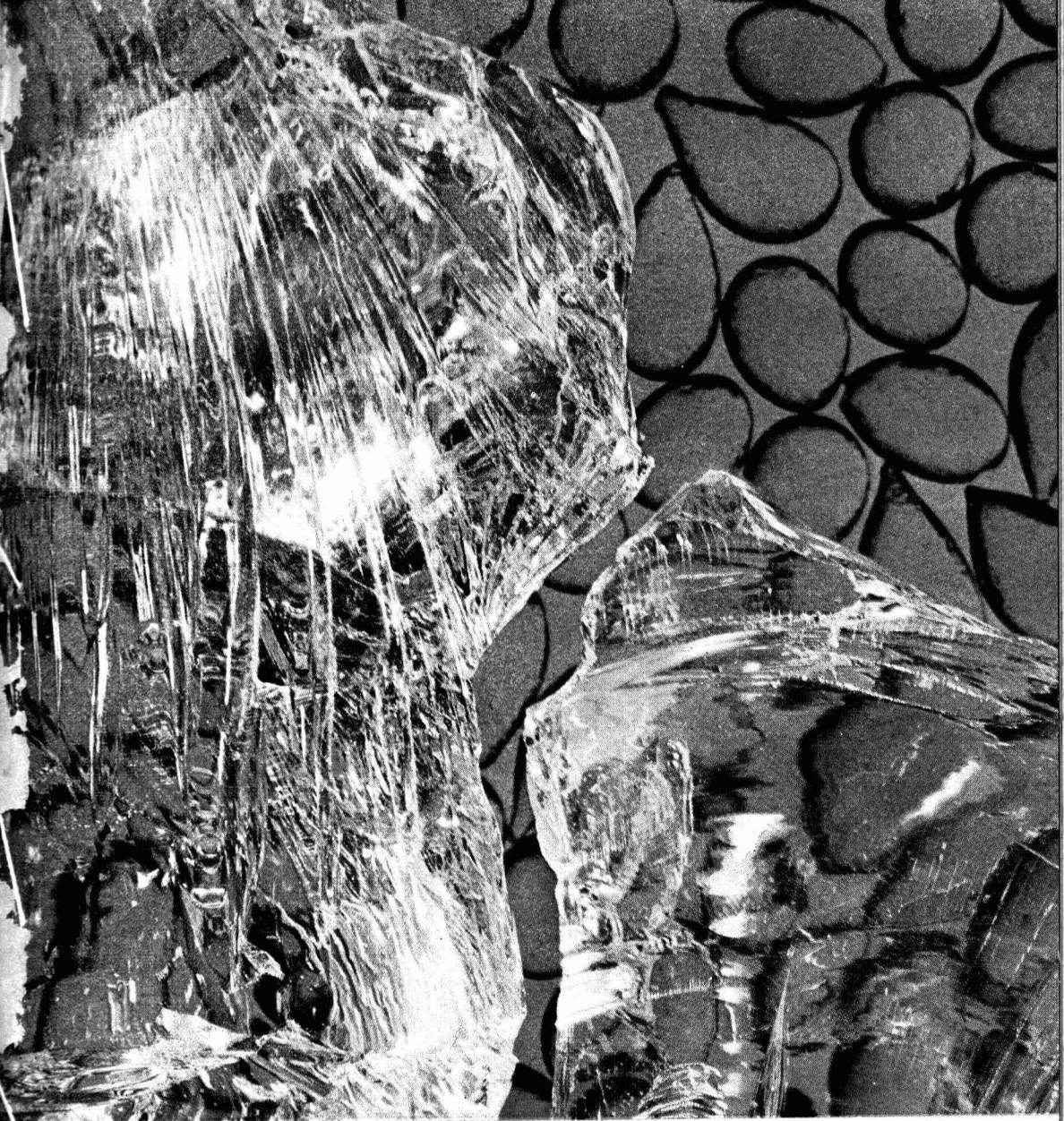
**EMULSION CHEMIST/TECHNOLOGIST** urgently required by manufacturers of **MAGICOTE** for development work on emulsion paints for the decorative market. Appropriate bench experience essential. Modern well equipped laboratories. Excellent salary and conditions. Applications in writing please to Personnel Officer, Lewis Berger (GB) Ltd., Freshwater Road, Dagenham, Essex.

### AGENCIES WANTED

**MANUFACTURERS, EXPORTERS AND BUYING AGENTS, NIGERIA** import firm intends to extend and promote Trade contracts with British Manufacturers and Exporters of **PAINT**. Manufacturers, Exporters and Buying Agents, please send your CIF Price Lists and Representative samples directly to Messrs: **A. F. ODUNSI BROTHERS**, PO Box 1243, IBADAN, NIGERIA, WESTERN NIGERIA.

**MORE CLASSIFIED ADVERTISEMENTS OVERLEAF**





**BASF**

## KETONE RESIN N

**Raw Materials  
for the  
Surface Coating  
Industry**

THROUGH



A completely synthetic, light-fast, chemical-resistant, unsaponifiable resin. Particularly suitable for light-coloured oil paints, alkyd enamels, and nitrocellulose lacquers, yielding coatings with high resistance to weathering. Literature is avail-

able on request, and our technologists are always ready to advise you.

Badische Anilin- & Soda-Fabrik AG  
Ludwigshafen am Rhein  
(West Germany)

2955

Distributors in the United Kingdom:

**Allied Colloids Limited**

Cleckheaton Road, Low Moor, Bradford, Yorkshire

Telephone: Bradford 78311

LAKE & PIGMENT  
**COLOURS**

*for*  
PAINTS  
PRINTING INKS  
CELLULOSE FINISHES  
LINOLEUM, LEATHERCLOTH  
ETC.

*We invite your enquiries*

**HORACE CORY**  
& CO. LTD.

**NATHAN WAY,  
WOOLWICH INDUSTRIAL ESTATE  
LONDON, S.E.18**