JOURNAL
OF THE
OIL AND COLOUR CHEMISTS' ASSOCIATION

Vol. 51 No. 5 May 1968

OCCA 20 REVIEW

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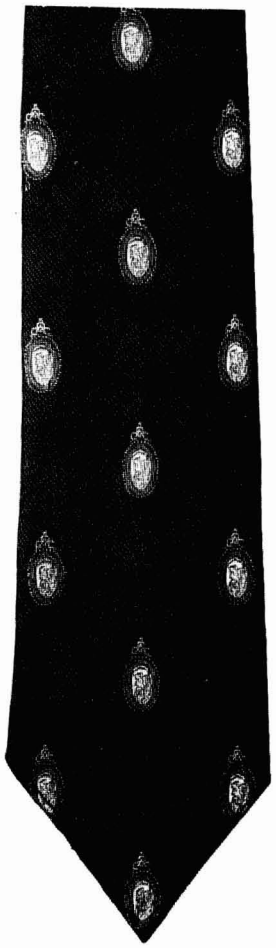

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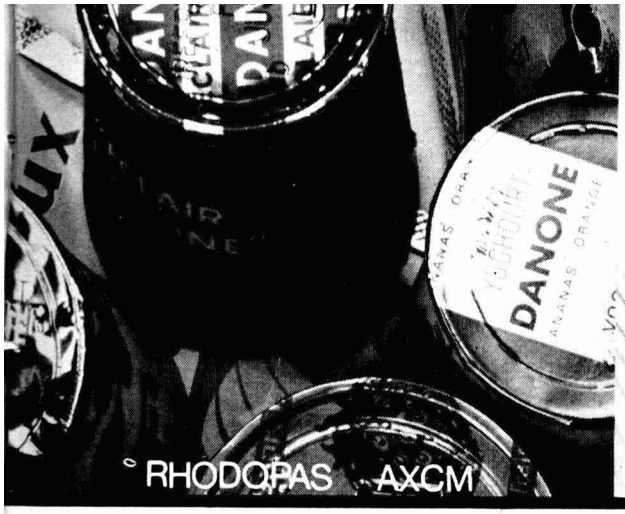

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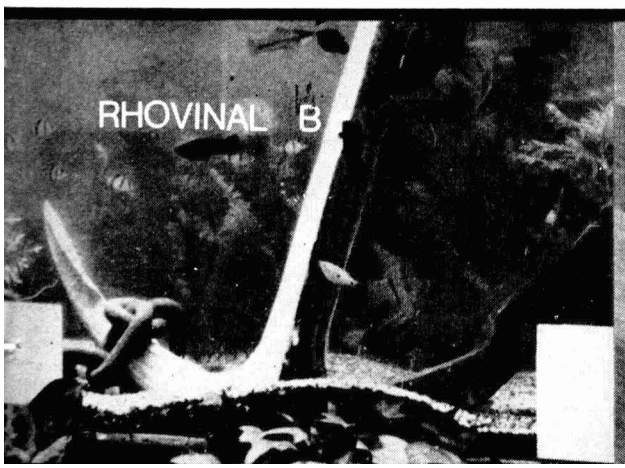

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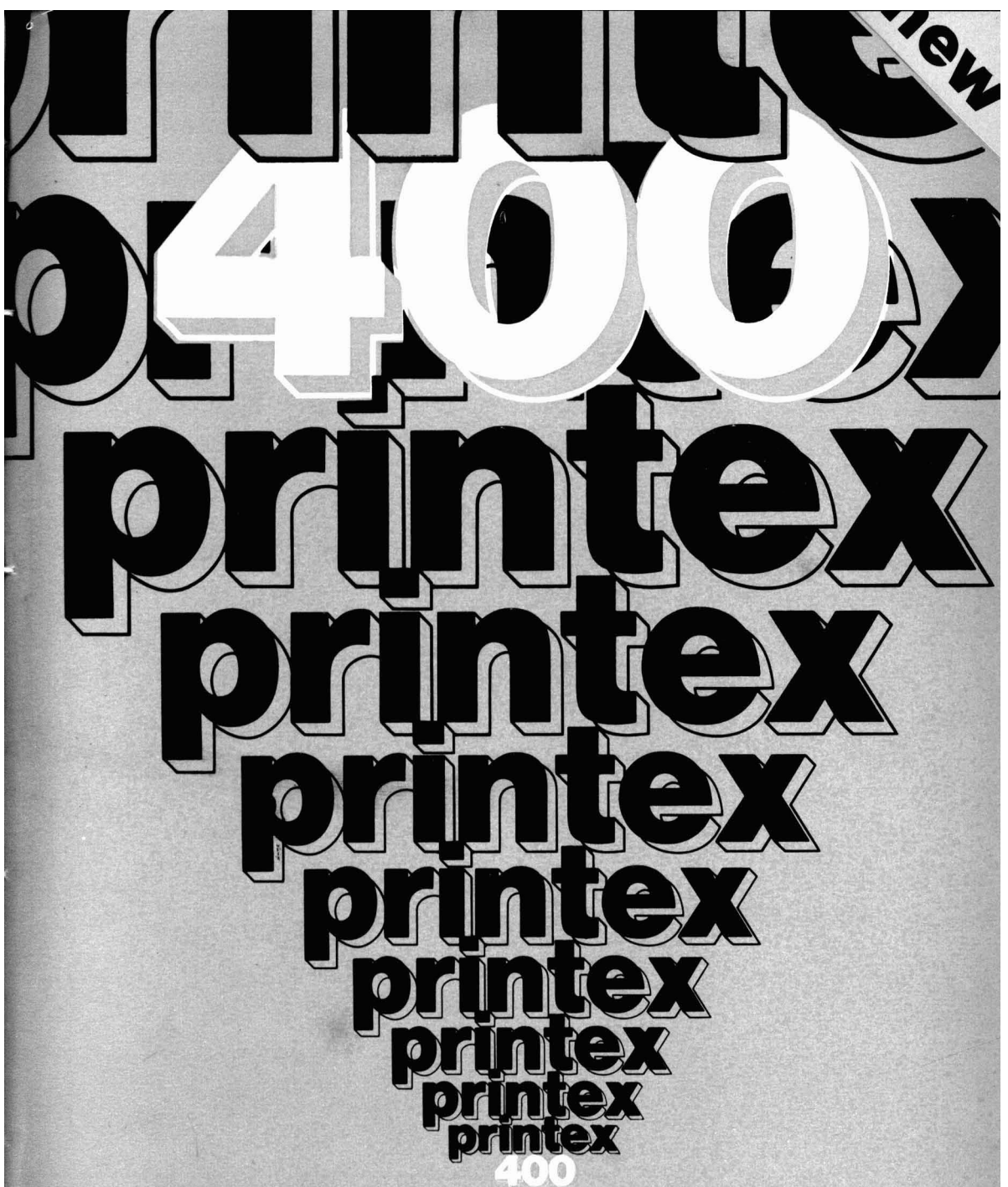

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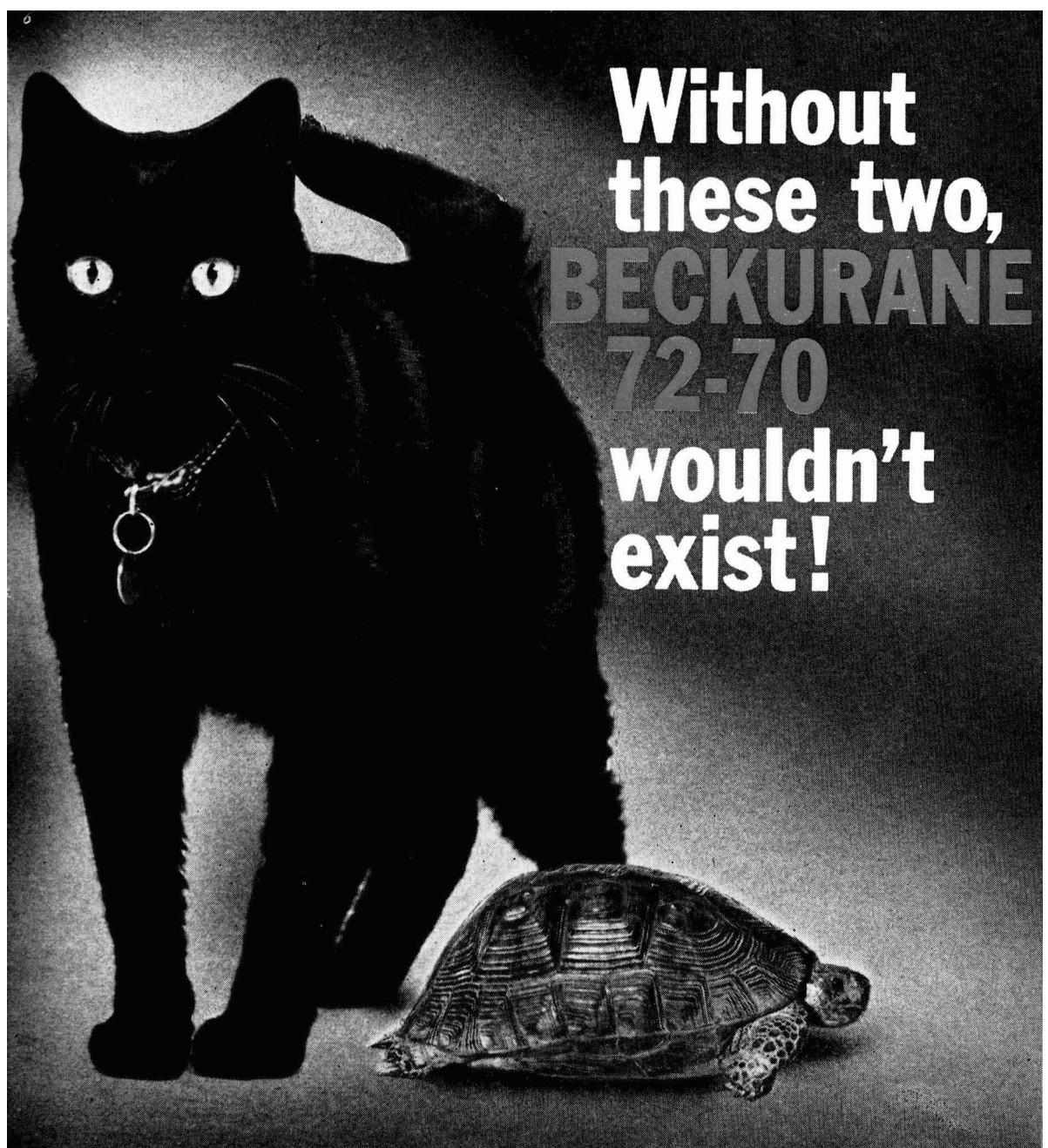

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Editorial correspondence should be addressed to the Hon. Editor, *JOCCA*, Cray Valley Products Ltd., St. Mary Cray, Kent.

General correspondence should be addressed to :

R. H. Hamblin, M.A., F.C.I.S., F.C.C.S.,
Director & Secretary,
Oil & Colour Chemists' Association,
Wax Chandlers' Hall, Gresham Street,
London, E.C.2. (Tel. : 01-606 1439)

Assistant Secretary : R. P. Bell, A.C.I.S.

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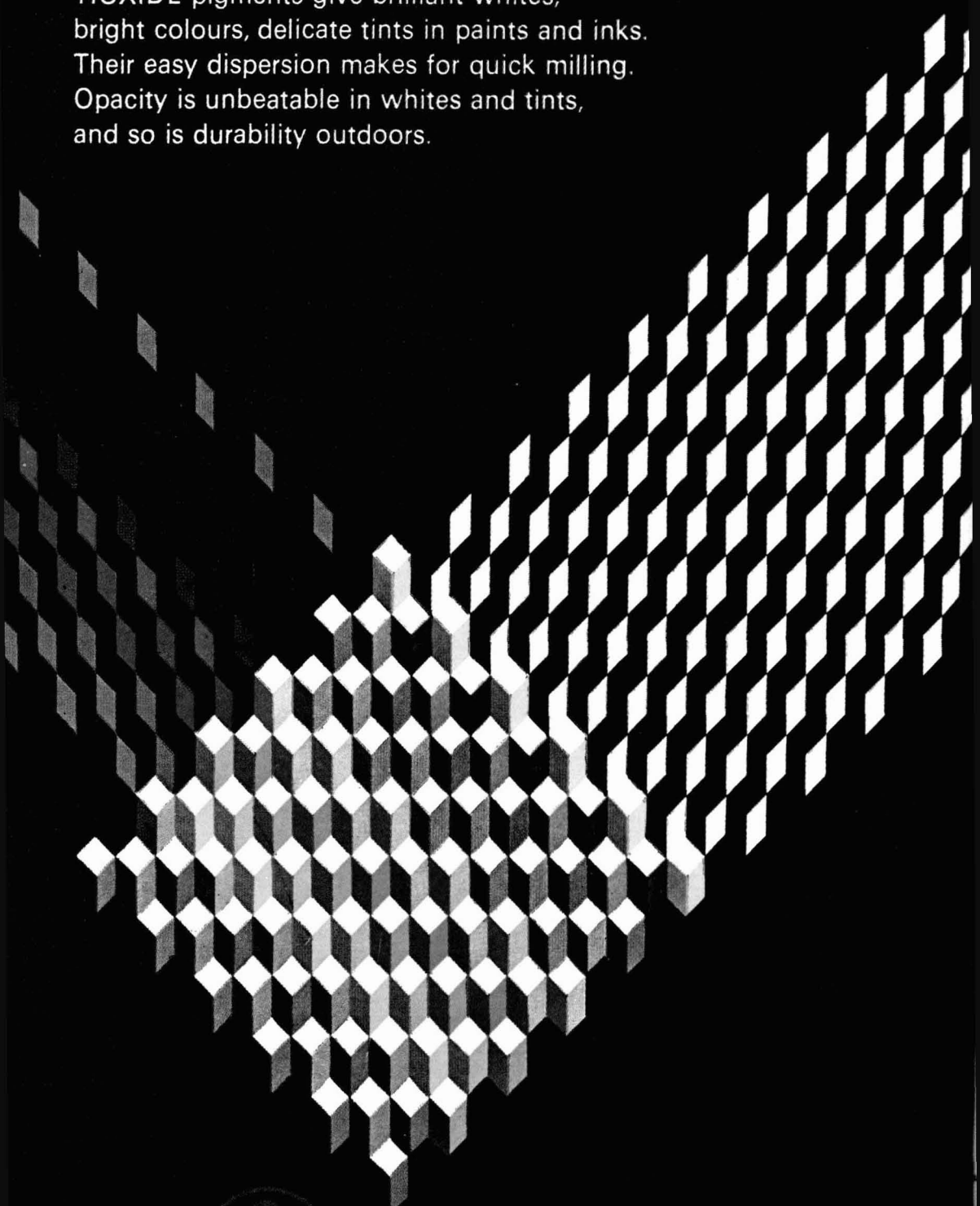

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Transactions and Communications

New oils and fatty acids for surface coating resin manufacture*

By K. B. Gilkes* and T. Hunt†

*BP Chemicals (UK) Ltd., Plastics Dept., Sully, Penarth, Glamorgan

†BP Chemicals Ltd., Polymer Unit, Sully, Penarth, Glamorgan

Summary

This paper is a review of some of the recent developments in the field of oils and fatty acids for the manufacture of surface coating resins. Materials for both air-drying and stoving systems are considered. They are arranged under the following headings.

1. New conventional fatty acids.
2. New synthetic acids.
3. New drying oils derived from conventional drying oil fatty acids.
4. Synthetic alternatives to conventional drying oils.

Nouvelles huiles et acides gras destinés à la fabrication de résines pour revêtements superficiels

Résumé

Dans cet article on passe en revue quelques développements récents dans le domaine d'huiles et d'acides gras utilisés dans la fabrication de résines pour revêtements superficiels. On considère, à l'égard des systèmes séchant à l'air ou au four, des constituants que l'on dispose sous les rubriques suivantes:

1. Nouvels acides gras conventionels.
2. Nouvels acides synthétiques.
3. Nouvelles huiles siccatives dérivées des acides gras d'huiles siccatives conventionelles.
4. Matières synthétiques alternatives aux huiles siccatives conventionelles.

Neue Öle und Fettsäuren zur Fabrikation von Harzen für Anstrichmittel

Zusammenfassung

In dieser Abhandlung wird eine Übersicht der neuesten Entwicklungen auf dem Gebiet der Öle und Fettsäuren für die Herstellung von Harzen für Anstrichmittel gebracht. Es werden sowohl Produkte, die sich für luft-wie auch ofentrocknende Systeme eignen, besprochen. Die Anordnung ist wie folgt:

1. Neuere Fettsäuren herkömmlicher Art.
2. Neue synthetische Säuren.
3. Neue trocknende Öle, die aus Fettsäuren trocknender Öle herkömmlicher Art gewonnen wurden.
4. Synthetische Alternativen für trocknende Öle herkömmlicher Art.

*Presented at a joint meeting of the Bristol Section and the Birmingham Paint, Varnish and Lacquer Club on 2 November 1967.

Новые масла и жирные кислоты для производства смольных поверхностных покрытий

Резюме

Обзор некоторых новейших развитий в области масел и жирных кислот для производства смольных поверхностных покрытий. Рассматриваются материалы для систем воздушной и печной сушки, которые обсуждаются под следующими заголовками

1. Новые общепринятые жирные кислоты.
2. Новые синтетические кислоты.
3. Новые быстровысыхающие масла получаемые из обычных жирных кислот быстровысыхающих масел.
4. Синтетические варианты общепринятых быстровысыхающих масел.

Introduction

In the last few years a great number of new raw materials have been made available to the surface coating resin manufacturer. A selection of the more important materials is discussed in the following paper from both a theoretical and a practical viewpoint.

New conventional fatty acids

Scandinavian tall oil fatty acids of low rosin content

It is only in the last four or five years that highly refined tall oil fatty acids of Scandinavian origin have become freely available, although high quality tall oil fatty acids of American origin have been available to resin producers for a much longer time. By high quality is meant material containing no more than 4 per cent of rosin acids. To explain why Scandinavian tall oils have assumed such importance as replacements for drying oils in long oil length alkyds, one must examine the chemical composition of these products and some typical analyses are shown in Table 1.

Table 1

Typical fatty acid compositions of some common drying oils and fatty acids

Oil or Fatty acid	Linoleic acid (%)	Oleic acid (%)	Linolenic acid (%)	*cis* 5,9, 12 Octa-deca-trienoic acid (%)	Rosin acids (%)	Saturated acid (%)
Linseed oil	24.0	21.0	45.0	—	—	10.0
Soyabean oil	52.5	31.5	3.0	—	—	13.0
Sunflower seed oil ..	58.0	34.0	—	—	—	8.0
Safflower seed oil ..	75.0	12.0	1.0	—	—	12.0
Tall oil fatty acids (American origin)	43.0	51.0	—	3.0	1.0	2.0
Tall oil fatty acids (Scandinavian origin)	49.5	39.5	—	8.0	1.0	2.0

It will be seen from the table that only the two tall oil fatty acids contain *cis* 5, 9, 12-octadecatrienoic acid. This is a non-yellowing isomer of linolenic acid and its triple unsaturation would be expected to give rapid autoxidation[1].

The rate of autoxidation of a long oil alkyd is related to the ratio of doubly and triply unsaturated acids in the oil (as these autoxidise) to mono unsaturated and saturated acids (which do not autoxidise to any great extent).

From the table it can be seen that the combined percentage of autoxidisable acids, i.e. *cis* 5, 9, 12-octadecatrienoic and linoleic is considerably greater in tall oil fatty acids of Scandinavian origin than in those of American origin. This explains the superior drying performance of long oil alkyds made from the Scandinavian material.

Comparing the Scandinavian tall oil fatty acids with the semi-drying oils in the table, the quantity of drying acids present is similar for the Scandinavian tall oil, soyabean oil and sunflower seed oil, whilst that of safflowerseed oil is considerably greater. However, it has been found that if the oil in a safflower seed oil-based alkyd is replaced by the equivalent amount of Scandinavian tall oil fatty acid and glycerol, resins which dry under normal conditions as well as the original safflower seed oil alkyds are produced, and these are significantly superior in drying performance to similar soyabean and sunflower seed oil based alkyds.

Certainly, the poorer drying of soyabean oil may be due to the presence of tocopherols[2], but this explanation is not satisfactory for sunflower seed oil, which contains a negligible quantity of these phenolic antioxidants. It is suggested that the extremely good autoxidation properties of the previously mentioned *cis* 5, 9, 12-octadecatrienoic acid, which is present as approximately 10 per cent of the Scandinavian tall oil fatty acids, contributes greatly to their outstanding drying properties.

Of course, drying performance is not the only factor to be considered when manufacturing alkyds for high quality decorative paints. Alkyds based on Scandinavian tall oil fatty acids of the type shown in the table have been shown to give exterior exposure results, over a period of 16 months, equal in all respects to soyabean oil or safflower seed oil based alkyds. For example, Fig. 1 shows the gloss retention of three long oil alkyds. These have the same formulation, the only difference being the oil used.

It can be seen, therefore, that the use of Scandinavian tall oil fatty acids as a raw material in long oil non-yellowing alkyds gives equal performance in this respect to the seed oils normally used. These acids have the added advantage of not being subject to the large price fluctuations that can occur with seed oils, which are dependent on size of harvest, weather conditions etc.

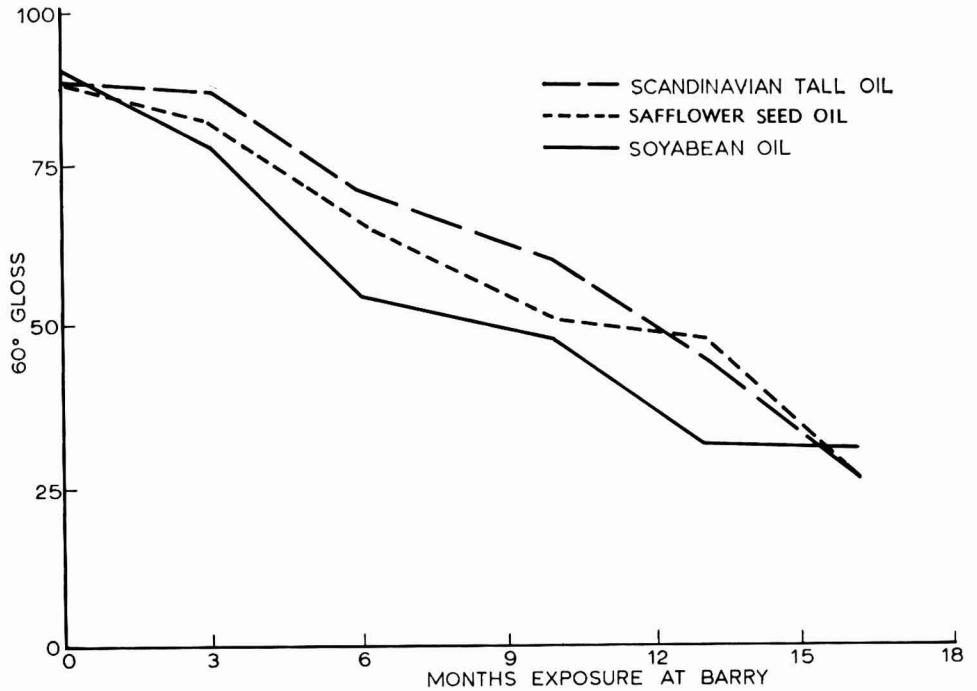


Fig. 1. Gloss retention of various long oil alkyds

New conjugated fatty acids

Until recently, there were only three types of conjugated drying oils and fatty acids available:

(i) natural conjugated drying oils (e.g. tung oil).

(ii) dehydrated castor oil and the corresponding fatty acids.

(iii) isomerised drying oils.

A new process has made it possible to convert linoleic and linolenic acid esters to their conjugated isomers in high yield and these materials are now available as the methyl esters or as the free acids. The manufacturers (J. Bibby & Sons Ltd.), claim a 95 per cent conversion to the conjugated form. Thus:

$CH_3(CH_2)_4\ CH{=}CH-CH_2CH=CH(CH_2)_7COOCH_3$ linoleic acid methyl ester

$$\downarrow$$

$$\left.\begin{array}{l} CH_3(CH_2)_4CH_2-CH=CH-CH=CH(CH_2)_7COOCH_3 \\ CH_3(CH_2)_4CH=CH-CH=CH-CH_2(CH_2)_7COOCH_3 \end{array}\right\}$$ ca 50 per cent of each

$CH_3CH_2CH=CH\ CH_2CH=CH-CH_2CH=CH(CH_2)_7\ COOCH_3$ linolenic acid methyl ester

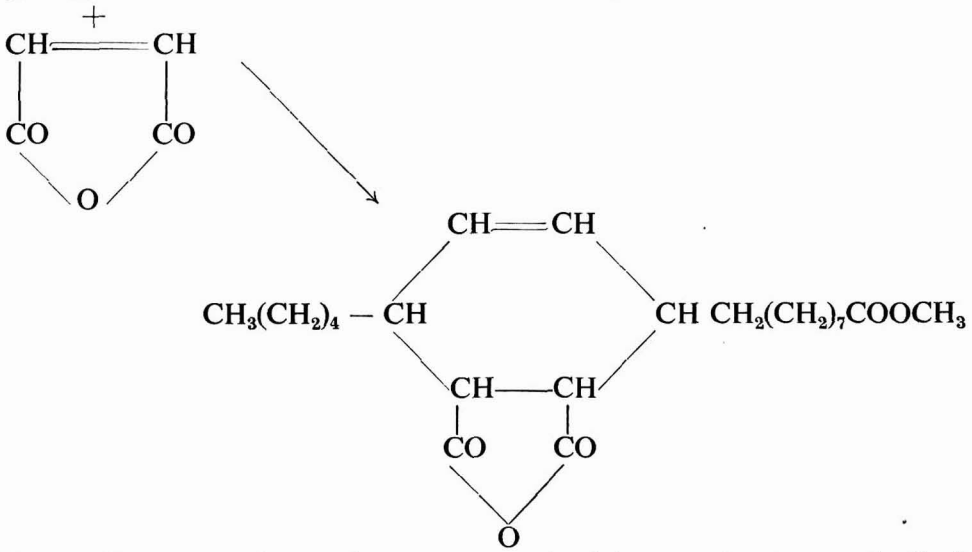
$$\downarrow$$

$$\left.\begin{array}{l} CH_3CH_2CH=CH\ \ CH=CH\ \ CH_2CH_2CH=CH\ (CH_2)_7COOCH_3 \\ CH_3CH_2CH=CH\ CH_2CH_2CH=CH\ CH=CH\ \ (CH_2)_7COOCH_3 \\ CH_3CH_2CH_2CH=CH\ CH=CH\ CH=CH\ CH_2\ (CH_2)_7COOCH_3 \end{array}\right\}$$

For alkyd manufacture, the methyl ester is heated with polyol in the presence of litharge or a similar catalyst. Methanol is evolved and the amount produced can be used to follow the progress of the reaction. Temperatures in the range 150-250°C are required. The alkyds are claimed to have good non-yellowing properties and, it is claimed, do not suffer from the after tack associated with the use of DCO fatty acids.

The conjugated esters copolymerise readily with vinyl monomers such as styrene, and they also undergo Diels-Alder reactions with maleic anhydride, cyclopentadiene etc. The reaction products with maleic anhydride are available from the same supplier. A typical structure is:

$CH_3(CH_2)_4\ CH{=}CH\ CH{=}CH\ CH_2(CH_2)_7COOCH_3$

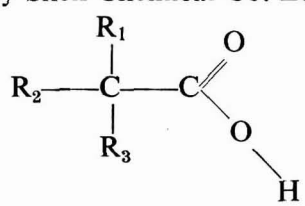


These adducts can be used to prepare plasticisers, polyesters and alkyd resins, by reaction of the anhydride groups with long chain alcohols, glycols etc. Water soluble plasticising alkyds have also been described[3].

New synthetic acids

Several saturated fatty acids in the C_6—C_{12} range have been introduced in the last few years for use in plasticising alkyds, e.g. capric, caprylic, pelargonic and heptanoic acids. These have been claimed to give improved performance over the traditional lauric and coconut fatty acids. However, the more recently introduced branched chain fatty acids with a predominantly tertiary acid structure, and their glycidyl esters, have, in the authors' experience, made possible further improvements to overall performance.

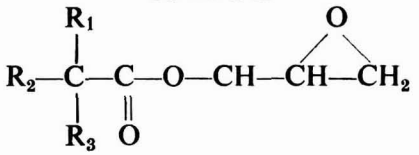
An example, offered by Shell Chemical Co. Ltd., may be represented as



R_1, R_2 and R_3 are aliphatic side chains giving the molecule a total number of carbon atoms between 9 and 11. The major component acids contain tertiary carbon atoms adjacent to the —COOH group.

The highly branched structure of these acids leads to steric hindrance and they do not esterify readily, even using high temperatures and prolonged reaction times. To overcome this problem, the glycidyl ester has been introduced:

Cardura E



It has been claimed[4], and these claims have been substantiated by the authors, that stoved films of excellent hardness, flexibility, initial gloss, gloss and colour retention on overstoving, and chemical resistance can be obtained by use of mixtures of plasticising alkyds based on these materials and melamine formaldehyde resins.

It is probable that the particularly good colour retention of the alkyds is due to the synthetic nature of the acid. This means it contains no natural organic material with trace unsaturation, which can be present even in high quality commercial saturated fatty acids and which could cause discoloration on overstoving.

It is felt though that the claim of excellent chemical resistance used to describe all tertiary acid modified alkyds needs qualification, as work carried out by one of the authors tends to show that the chemical resistance, especially caustic soda resistance, depends as much on the overall alkyd formulation as on the incorporation of the tertiary acid in the polymer molecule.

Esters of these acids, including the glycidyl ester, are extremely difficult to hydrolyse as a result of the tertiary acid structure. However, the use of the glycidyl ester does not automatically give alkyds with excellent alkali resistance,

Table 2

Comparison of several Cardura E containing plasticising alkyds

Resin	Composition % w/w						5% NaOH at 80°C. Hours to film breakdown
	CE	PA	AA	G	PE	TEG	
A	50.8	40.9	—	8.3	—	—	14
B	48.8	41.5	—	9.7	—	—	7
C	45.0	33.0	11.0	11.0	—	—	2
D	56.3	28.2	9.9	—	5.6	—	12
E	29.3	44.3	—	—	6.5	20.1	2
F	Commercial pelargonic acid based alkyd						7

Key CE = Cardura E PA = Phthalic anhydride
AA = Adipic acid PE = Pentaerythritol
G = Glycerol TEG = Triethylene glycol

as the polyol-polycarboxylic acid ester groups formed by the other components in the alkyd are still liable to attack. Careful formulation can give outstanding alkali resistance, but minor variations in composition, or procedure, can result in stoved films with considerably lower resistance to alkalis. This is illustrated in Table 2, which compares several laboratory formulations with a commercial pelargonic acid alkyd.

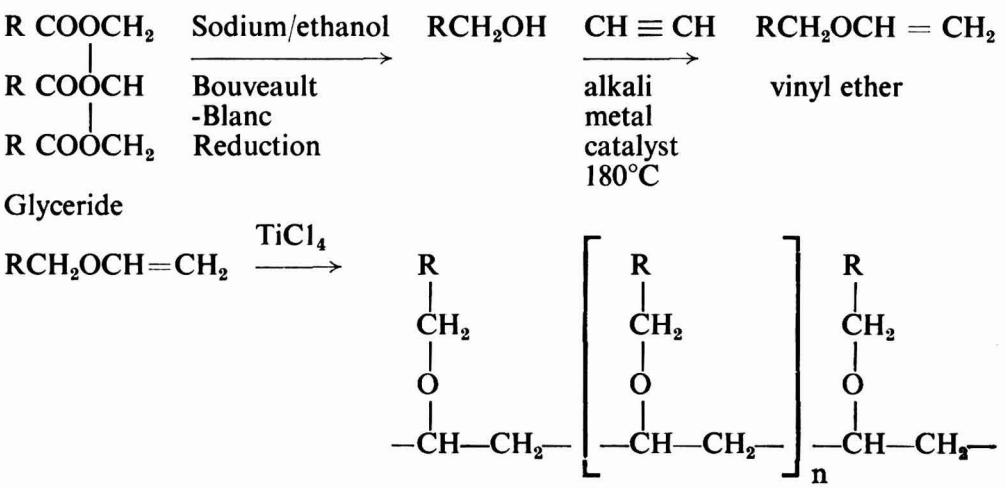
The acid values of all the resins were between 6 and 12 mg. KOH/g. A 3 : 1 ratio alkyd/melamine resin (Epok U9192) was used. The pigment/binder ratio was 0.8 : 1 and the films were stoved for 30 minutes at 120°C, on Bonderite 55 steel panels.

New drying oils derived from conventional drying oil fatty acids

Polyvinyl ethers of drying oil alcohols

Drying oil modified alkyd resins contain large numbers of hydrolysable ester groupings and consequently the air dried films have relatively poor alkali resistance. Workers in the USA have shown that useful coating materials can be prepared by polymerising vinyl ethers of drying oil alcohols[5, 6]. The polymers do not contain any easily hydrolysable ester groups and both air dried and stoved films are said to have good resistance to alkalis.

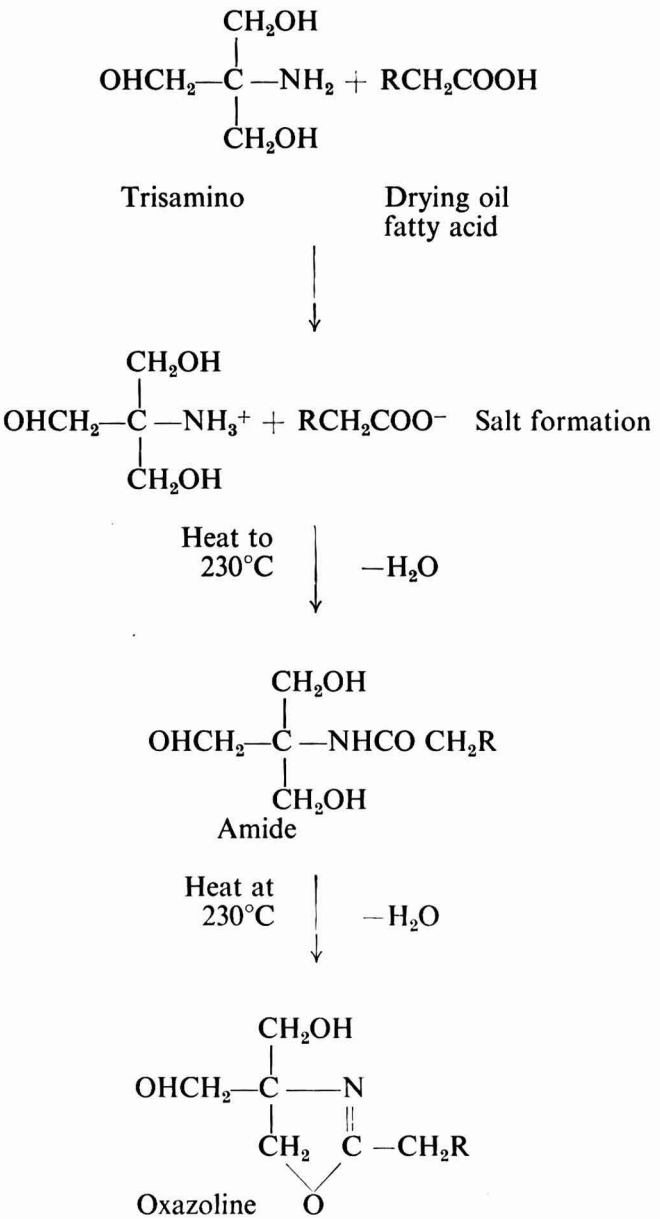
The drying oil alcohols are prepared from the corresponding glycerides by Bouveault-Blanc reduction and they are then reacted with acetylene in the presence of an alkali metal catalyst to give the vinyl ether. This readily polymerises when treated with Friedel Crafts catalysts such as $TiCl_4$ to give colourless, viscous oils. Copolymers with styrene, using free radical catalysts, have also been described. The following are the reactions involved in the preparation of a vinyl ether homopolymer.

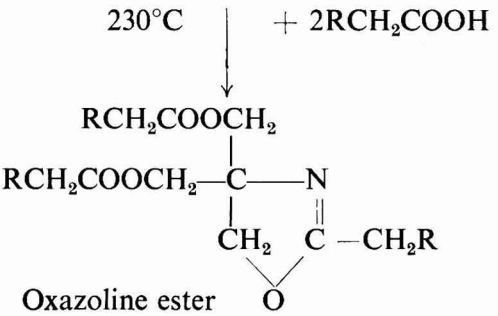


It appears that coatings based on this type of polymer are not being marketed, and this suggests that their performance is not sufficiently good to compensate for their relatively high cost. Certainly some work in which the writers' laboratories were involved showed that autoxidation of the drying oil residues led to alkali sensitive products, so the absence of ester groups from an autoxidizable resin does not necessarily guarantee alkali resistance in the cured film.

Vinyl oxazoline esters

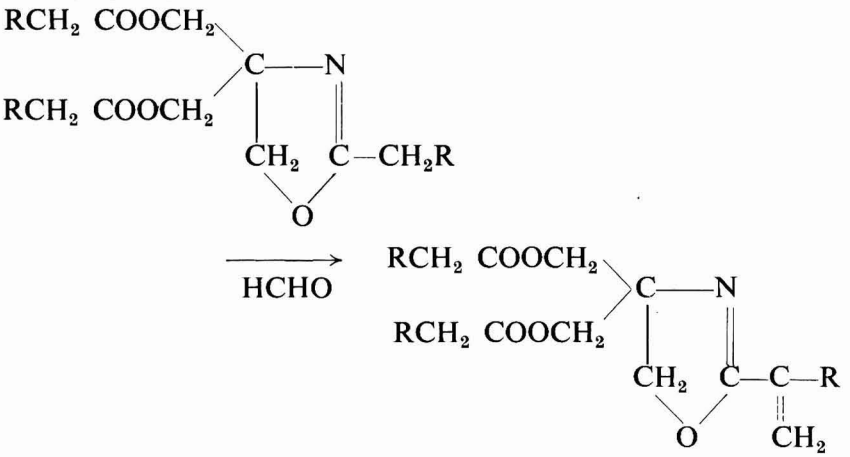
Another class of new raw materials that can be used to prepare oils and resins which are claimed to have improved alkali resistance comprises the reaction products of β-amino alcohols and drying oil fatty acids. When a β-amino alcohol is heated with a drying oil fatty acid, the initially formed amide undergoes ring closure to give an oxazoline. The following are the reactions taking place when the amino alcohol is trishydroxymethyl amino methane (Trisamino).





Oxazoline ester

The oxazoline ester can be reacted with paraformaldehyde to give a polymerisable vinyl group thus:



vinyl oxazoline ester

The vinyl group can be readily homopolymerised or copolymerised with styrene, etc., using free radical catalysts. The products are light-coloured oils or resins that will air dry to tough films. The films are said to be superior to those obtained from styrenated alkyds, as styrenation takes place at the vinyl group, leaving the drying oil unsaturation intact. Table 3 compares the alkali resistance

Table 3

Comparison of styrenated vinyl oxazoline ester with some commercial alkyds

Resin	Effect of spotting clear films with 10% NaOH solution	
	1-day-old films	7-day-old films
Alkyd	Loss of gloss and some yellowing after 10min. Softening	All films were severely attacked after 10min exposure
VT-modified alkyd	Yellows immediately. Blisters after 10min	
Styrenated VOE	Film unmarked but slightly softened	

of a commercial high build, high quality decorative alkyd, a commercial vinyl toluene modified alkyd and a styrenated vinyl oxazoline ester containing 20 per cent combined styrene. The drier level used in each case was 0.4 per cent Pb, 0.1 per cent Ca and 0.03 per cent Co on solid resin.

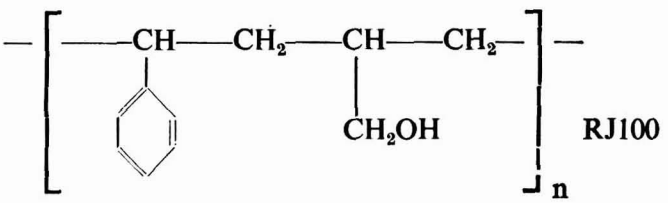
The seven-day-old films were also spotted with xylol. The VT-modified alkyd and the styrenated VOE blistered instantly; the unmodified alkyd was unaffected after ten minutes exposure. These results do not indicate that the oxazoline ester resin has any striking advantage over a conventional alkyd.

A vinyl oxazoline ester prepared from Trisamino and tall oil fatty acids is now available commercially and this was used to prepare the resin described in Table 3. It is claimed that the unpolymerised material can be used to modify exterior latex paints, giving improved adhesion and higher solids[7].

Drying oil fatty acid esters of polymeric polyols

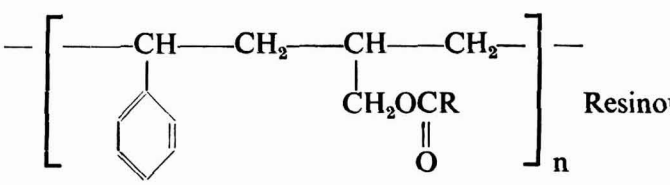
Normal glyceride drying oils have to be heat bodied or incorporated into alkyd resins to give reasonable drying properties. If a polymeric polyol is esterified with drying oil fatty acids, one obtains a relatively high molecular weight drying oil which will give acceptable drying speeds without further modification. Probably the most interesting oils of this type are derived from the styrene/allyl alcohol copolymers (such as RJ100 ex Monsanto Chemicals Ltd.)

RJ100 is a colourless, brittle solid with a molecular weight of approximately 1,600 and a hydroxyl equivalent weight of 300. It esterifies readily with drying oil fatty acids at temperatures above 200°C. Products of this type have been recommended for use in stoving primers for metal. A typical drying oil fatty acid ester preparation may be represented as follows.



RJ100

Linseed oil fatty acids (RCOOH). Heat slowly to 250°C under N_2 and hold until theoretical quantity of water distils.



Resinous ester

Water thinnable resins based on RJ100 have also been developed[8]. These are prepared by fully esterifying the polyol with a drying oil fatty acid, then heating

the resulting ester at 220°C with maleic anhydride. The maleic adduct gives water dilutable salts when neutralised with ammonia or organic amines. Formulations of this type are being recommended for use in stoving primers, particularly for application by electrodeposition.

Films of both types of RJ100 formulations described have shown excellent alkali resistance compared with a conventional alkyd.

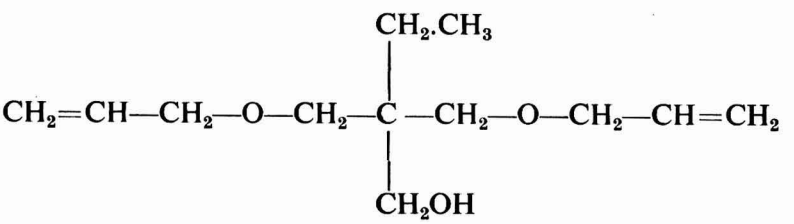
Synthetic alternatives to conventional drying oils

Allyl ethers

A large amount of research has been carried out on the utilisation of these compounds in surface coatings, especially as replacements for drying oils[9], the great advantage of allyl ethers being that they can give completely non-yellowing oxidised films.

It has been found[10] that allyl ethers autoxidise in a somewhat different manner from drying oils. For example, they take up much less oxygen during oxidation than drying oils.

A typical compound of the allyl ether type is trimethylol propane diallyl ether (TMPDAE) which is available in commercial quantities.



Interesting surface coatings can be made by incorporating the allyl ether groups, of trimethylol propane diallyl ether for example, into a normal alkyd by reacting the free hydroxyl group with polycarboxylic acids. It appears from earlier work[10] that complete replacement of drying oils by allyl compounds in an alkyd gives air-dried films which, although very hard, embrittle on ageing. This is a serious fault and it is possible that the compromise of partial replacement of drying oil by allyl ether would give more acceptable durability, whilst still incorporating the advantages bestowed by the allyl ether groups. The performance of a resin of this type made from trimethylol propane diallyl ether, phthalic anhydride, trimethylol propane and tall oil fatty acids is compared with a standard medium oil length linseed alkyd in Table 4.

The experimental alkyd contained 27 per cent phthalic anhydride, 34.5 per cent fatty acid and 26 per cent trimethylolpropane diallyl ether.

It would appear that some improvement in overall properties is shown, but probably not sufficient to merit the use of the expensive allyl ether compound.

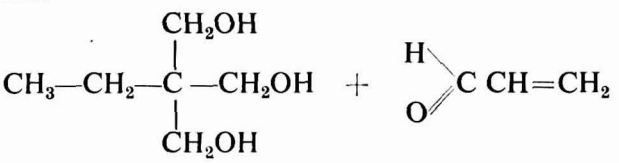
Table 4

Results of paint evaluation of TMPDAE modified alkyd and medium oil length linseed alkyd

Test	Performance	
	Medium oil length linseed alkyd	TMPDAE alkyd
(a) Tests on scuffed aluminium after seven days air-drying		
Adhesion	100%	100%
Mar resistance	Fair	Fairly good
Pencil hardness	B	F
(b) Tests on unscuffed mild steel after air-drying		
Adhesion	20%	10%
Mar resistance	Fair	Fair
Pencil hardness	6B	B
(c) Yellowing		
Exposed to $(NH_4)_2CO_3$ overnight after 24 hours air-drying	Heavy yellowing	Trace yellowing

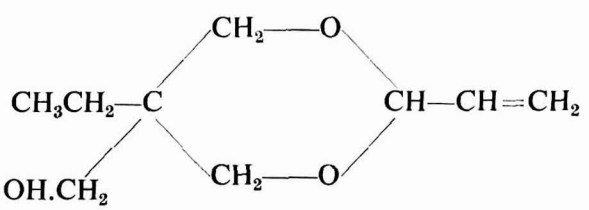
Vinyl cyclic acetals

A considerable amount of work has been carried out by Du Pont on the reaction products of acrolein and substituted acroleins with various polyhydric alcohols, particularly trihydric alcohols[11]. These reaction products are of considerable interest, as the allylic grouping is capable of autoxidation and subsequent polymerisation. The preparation of a typical compound of this type is shown below.



1, 1, 1—Trimethylol propane Acrolein

Oxalic acid catalyst. Reflux in hexane, removing water of reaction. Purify by distillation.



5–ethyl–5- hydroxymethyl–2 vinyl–1, 3-dioxane.

The incorporation of these compounds into a polymer molecule presents difficulties as the vinyl group tends to react with carboxyl groups more readily than the hydroxyl group. This problem has been solved by ester interchange techniques[11] with, for example, methyl methacrylate/ethyl acrylate copolymers[12].

Commercialisation of resins containing these vinyl substituted cyclic acetals does not appear to be imminent, presumably because their overall performance does not justify their high price, but they are of interest since they show how air-drying properties can be obtained from chemical structures far removed from the traditional drying oils mentioned at the start of this paper.

Acknowledgment

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Calculation of paint formulations by computer

By E. Hoffmann and J. Spencer

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

Summary

The use of a computer for the calculation of the more complicated paint formulations is recommended. Two examples are given to illustrate the advantages of the procedure.

Le calcul par ordinateur des formulations de peintures

Résumé

On conseille l'emploi d'un ordinateur pour calculer les plus complexes formulations de peintures. On cite deux exemples afin de démontrer les avantages du procédé.

Die Berechnung von Anstrichmittelrezepturen Mittels Computer

Zusammenfassung

Der Einsatz eines Computers für die Berechnung der komplizierteren Anstrichmittelrezepturen wird empfohlen. An zwei Beispielen werden die Vorteile dieser Arbeitsweise dargestellt.

Расчет красочных формуляций при помощи вычислительных машин

Резюме

Рекомендуется применение вычислительной машины для расчета более сложных красочных формуляций. Прилагаются два примера иллюстрирующие преимущества такого применения.

Introduction

The computation of paint formulations to achieve, for instance, a given pigment volume concentration is usually straightforward and is not very time consuming. However, more complicated cases are sometimes encountered, the solution of which would be excessively time-consuming if the calculations were carried out in the usual way, and in these instances good use can be made of a computer. This paper treats two cases which one of the authors encountered in his work on the formulation of fungus-resistant paints, and it is thought that a discussion of these may prove helpful to others.

Calculations

Case 1:

It was required to formulate a latex paint containing titanium dioxide and zinc oxide, the pigment volume concentration (PVC) and the zinc oxide concentration

on the solid content of the paint to be within the range of 40 to 50 per cent. The information to be obtained was:

(A) The titanium dioxide concentration compatible with these conditions.

(B) The cost of raw material per unit volume of such paints containing 55 per cent solids.

The following equations must be satisfied

$$\frac{4.26Y}{1.15R + 4.26Y + 5.47Z} = b \tag{1}$$

$$\frac{5.47Z}{1.15R + 4.26Y + 5.47Z} = c \tag{2}$$

$$\frac{Z + Y}{R + Z + Y} = a \tag{3}$$

where a = PVC
Y = Volume of titanium dioxide
Z = Volume of zinc oxide
R = Volume of resin
b = Weight fraction of titanium dioxide
c = Weight fraction of zinc oxide
Density of titanium dioxide = 4.26
Density of zinc oxide = 5.47
Density of resin = 1.15

Expressing R and Y in terms of Z

$$Z[5.47\,a - (1 + 1.28\,b/c)\,1.15\,c\,(1-a) - (1 + 1.28\,b/c)\,5.47\,ac + 1.53\,ab] = 0$$

from which

$$b = \frac{5.47\,a - 1.15\,c - 4.32\,ac}{1.47 + 4\,a} \tag{4}$$

To obtain the information under (A) each value of a between 0.40 and 0.50 in steps of 0.01 has to be combined with the range of allowed values of c.

The following array gives the combination:

a 0.40, 0.41 ..... 0.50

c
- 0.40, 0.40 ..... 0.40
- 0.41, 0.41 ..... 0.41
- 0.50, 0.50 ..... 0.50

There are 121 values altogether and it would be very time-consuming to calculate these by longhand.

The following steps have to be carried out to obtain the information under (B):

1. Calculate the total volume, V, of the solids in a paint for which Z is 1 for each combination of a and c in the array:

$$Y = 1.28\ b/c,\ R = \frac{(1-a)\ (1\ +\ 1.28\ b/c)}{a}$$

2. From the volume of the ingredients calculate the weight of each ingredient by multiplying by the corresponding density, and calculate the total weight.
3. Calculate the price of each ingredient by multiplying the weight by the price per unit weight and from this the total price. The prices per unit weight used in this calculation are: resin, 33 cents; titanium dioxide, 23 cents; zinc oxide, 13.5 cents.
4. From the total weight W of the solids calculate the volume of water u to be added to give a solid content of 55 per cent from the equation $W/(W + u) = 0.55$.
5. Dividing P by the total volume of solids + water $(V + u)$ gives the price per unit volume.

The calculations were programmed in the ALGOL language and run on a CDC 3200 computer of the CSIRO computing network. The total running time for the programme (including compilation) was 1min 42sec for the calculation of Case 1, and 2min 19sec for that of Case 2 (below).

The programme was written in such a way that the unit prices of the raw materials could easily be changed if required.

If the complete requirements of the finished product can be stated exactly a single solution to the problem can be obtained by linear programming methods, and standard programmes for such calculations can be found in the programme libraries of most computers. However, in the cases here dealt with, more information can be gained by calculating for the whole range of feasible compositions, so that the results may be used for selecting the most appropriate composition to fulfil a given requirement, and the effect of deviations from the optimum may be clearly seen.

From the table produced by the computer the set of values which are of interest can be found by inspection. For instance, with the conditions stated, the concentration of titanium dioxide in the paint film will range from 25 to 40 per cent. In the present case it was decided to keep the PVC between 40 and 45 per cent (to have a paint film of good washability) and, because of the hiding power required, it was desirable to have not less than 34 per cent titanium dioxide. There are 16 paint formulations which fulfil this condition, and the values are shown in Table 1 together with the values from steps 1 to 5.

Which of the formulations is adopted depends of course on the properties judged most important. Paint 1 probably will have the best washability, whereas paint 13 will have the best hiding power. The difference in cost of raw materials for these two cases is only 1.2 per cent.

Table 1

Case 1: Paint formulations containing at least 34 per cent titanium dioxide

	PVC	Weight fraction of ZnO	Weight fraction of TiO_2	Volume				Weight				Price (cents)				Volume of water for 55% solids	Total volume	Price per unit volume (cents)
				ZnO	TiO_2	Resin	Total	ZnO	TiO_2	Resin	Total	ZnO	TiO_2	Resin	Total			
1	0.40	0.40	0.34	1.00	1.08	3.12	5.20	5.47	4.60	3.59	13.66	73.85	105.85	118.42	298.11	11.18	16.38	18.20
2	0.41	0.40	0.35	1.00	1.10	3.03	5.13	5.47	4.71	3.48	13.66	73.85	108.26	114.95	297.05	11.18	16.31	18.21
3	0.41	0.41	0.34	1.00	1.05	2.95	5.00	5.47	4.47	3.39	13.33	73.85	107.74	111.88	288.47	10.90	15.90	18.14
4	0.42	0.40	0.35	1.00	1.13	2.94	5.07	5.47	4.81	3.38	13.66	73.85	110.61	111.57	296.07	11.18	16.24	18.22
5	0.42	0.41	0.34	1.00	1.07	2.86	4.93	5.47	4.57	3.29	13.33	73.85	105.03	108.59	287.46	10.90	15.84	18.15
6	0.43	0.40	0.36	1.00	1.15	2.85	5.01	5.47	4.91	3.28	13.66	73.85	112.90	108.77	295.01	11.18	16.18	18.23
7	0.43	0.41	0.35	1.00	1.09	2.78	4.87	5.47	4.66	3.19	13.33	73.85	107.26	105.38	286.48	10.90	15.78	18.16
8	0.43	0.42	0.34	1.00	1.04	2.70	4.74	5.47	4.43	3.11	13.01	73.85	101.89	102.62	278.36	10.64	15.39	18.09
9	0.44	0.40	0.37	1.00	1.18	2.77	4.94	5.47	5.01	3.18	13.66	73.85	115.13	105.06	294.03	11.18	16.12	18.24
10	0.44	0.41	0.36	1.00	1.12	2.69	4.81	5.47	4.76	3.10	13.33	73.85	109.44	102.25	285.53	10.90	15.71	18.17
11	0.44	0.42	0.35	1.00	1.06	2.62	4.69	5.47	4.52	3.02	13.01	73.85	104.01	99.51	277.43	10.64	15.33	18.10
12	0.44	0.43	0.34	1.00	1.01	2.56	4.57	5.47	4.30	2.94	18.71	73.85	98.84	97.02	269.71	10.40	14.96	18.03
13	0.45	0.40	0.37	1.00	1.20	2.69	4.88	5.47	5.10	3.09	13.66	73.85	117.31	101.92	293.07	11.18	16.06	18.25
14	0.45	0.41	0.36	1.00	1.14	2.61	4.75	5.47	4.85	3.01	13.33	73.85	111.56	99.19	284.60	10.90	15.66	18.18
15	0.45	0.42	0.36	1.00	1.08	2.55	4.63	5.47	4.61	2.93	13.01	73.85	106.08	96.60	276.52	10.64	15.27	18.11
16	0.45	0.43	0.35	1.00	1.03	2.48	4.51	5.47	4.38	2.85	12.71	73.85	100.85	94.13	268.82	10.40	14.91	18.03

Case 2:

It was required to formulate a latex paint containing titanium dioxide and zinc oxide as pigments and barium metaborate as a fungicidal additive, the following conditions being prescribed: zinc oxide not less than 40 per cent by weight on the solid content of the paint; barium metaborate content to be within the range 15 to 25 per cent on the solid content of the paint; pigment volume concentration within the range of 40 to 50 per cent. The information to be obtained was:

(A) The titanium dioxide concentration compatible with these conditions

(B) The cost of raw material per unit volume of these paints at 55 per cent solids concentration.

The following equations must be satisfied:

$$\frac{4.26\,Y}{1.15R + 4.26\,Y + 5.47Z + 3.3n} = b \tag{5}$$

$$\frac{5.47Z}{1.15R + 4.26\,Y + 5.47Z + 3.3n} = c \tag{6}$$

$$\frac{3.3n}{1.15R + 4.26\,Y + 5.47Z + 3.3n} = d \tag{7}$$

where n = Volume of barium metaborate
d = Weight fraction of barium metaborate
Density of barium metaborate 3.3
and the other variables are as before

Dividing equation (5) by (6)

$$Y = 1.28\ Z\ b/c \tag{8}$$

and dividing equation (7) by (6)

$$n = 1.66\ Z\ d/c \tag{9}$$

$$\frac{Z + Y + n}{R + Z + Y + n} = a \tag{10}$$

$$\frac{5.47Z}{1.15R + 5.47Z\ (1 + b/c + d/c)} = c \tag{11}$$

Using equations (8), (9), (10), and (11) to express R, Y, and n in terms of a, b, c, d and Z, and substituting the values in equation (5) gives

$$Z\left[\frac{5.47\ (1-Fc)}{1.15\ c} - \frac{E\ (1-a)}{a}\right] = 0$$

where $F=(1 + b/c + d/c)$ and $E=(1 + 1.28\ b/c + 1.66\ d/c)$

From this

$$b = \frac{5.47\ a - 4.32\ ac - 3.56\ ad - 1.15\ c - 1.91\ d}{1.47 + 4\ a} \tag{12}$$

To obtain the information required for (A) each value of a between 0.40 and 0.50 has to be combined with all the allowed values of c. The following array gives the combinations:

$$a \quad 0.40,\ 0.42 \ldots\ldots\ldots\ldots 0.50$$

$$c \begin{cases} 0.40,\ 0.40 \\ 0.42,\ 0.42 \\ 0.50,\ 0.50 \end{cases}$$

and each value of ac has to be combined with $d=0.15,\ 0.17\ldots\ldots 0.25$. There are 216 values altogether and the calculation was carried out in steps of 0.02 to reduce the number of values obtained.

To obtain the information for (B) the same steps have to be carried out as described for the previous case.

From the printout produced by the computer the set of values which are of interest are found by inspection. For example, if a paint with at least 20 per cent titanium dioxide on the solid content is required, the composition and cost of raw materials would be as shown in Table 2.

Table 2

Case 2: Paint formulations containing at least 20 per cent titanium dioxide

PVC	Weight fraction			Price per unit volume (cents)
	ZnO	TiO_2	$BaB_2O_4 . H_2O$	
0.44	0.40	0.21	0.15	17.82
0.46	0.40	0.22	0.15	17.84
0.46	0.42	0.20	0.15	17.69
0.46	0.40	0.20	0.17	17.78
0.48	0.40	0.23	0.15	17.85
0.48	0.42	0.22	0.15	17.71
0.48	0.44	0.20	0.15	17.56
0.48	0.40	0.21	0.17	17.80
0.50	0.40	0.25	0.15	17.87
0.50	0.42	0.23	0.15	17.72
0.50	0.44	0.21	0.15	17.58
0.50	0.40	0.23	0.17	17.81
0.50	0.42	0.21	0.17	17.67

Acknowledgment

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Binder design and performance in emulsion paints*

By C. Bondy

Revertex Ltd., E. Industrial Estate, Harlow, Essex

Summary

The significance of the glass transition temperature (T_g) for film formation and subsequent paint film behaviour is discussed. Data are presented showing the variation of T_g with copolymer composition in the case of selected monomer pairs.

Exposure to light causes cross-linking and degradation of polymeric binders. Measurement of changes in physical properties such as tensile strength, ultimate elongation, T_g, etc., during exposure permits predictions to be made concerning exterior durability of paints made with different resin binders.

The loss of film thickness during weathering can be used to obtain information on chalk resistance and durability of paints after relatively short periods of outdoor exposure.

Chemical, especially alkali, resistance depends very largely on copolymer composition. It can be assessed by accelerated tests.

The rheology of paints is discussed with particular reference to the particle size of the binder emulsion. The effect of thickeners and dispersants is briefly surveyed.

Composition et rendement du liant en peintures-émulsions

Résumé

On discute l'importance de la temperature de transition vitreuse (T) dans la formation de feuil et le comportement du feuil de peinture subséquent. On présente des données qui revélent la variation de T avec la composition du copolymère dans le cas de certaines paires de monomères.

Exposition à la lumière provoque la reticulation et la dégradation de liants-polymeres. Par la détermination des changements de propriétés physiques telles que résistance à la traction, allongement extrême, Y etc., lors de l'exposition, on peut faire des prédictions concernant la durabilité a l'extérieure des peintures contenant différentes résines-liants. On peut utiliser la perte de l'épaisseur de feuil au cours du vieillissement pour obtenir des indications sur la résistance au farinage et la durabilité des peintures après l'exposition a l'extérieure de durée assez courte.

La résistance aux agents chimiques, notamment aux alcalis se dépend en grande mesure de la composition du copolymère, et l'on peut la déterminer par des essais accélérés.

On discute la rhéologie de peintures à l'égard particulier de la granulométrie du liant-émulsion. On étudie brièvement l'effet des agents d'épaississement et de dispersion.

Planung und Leistungsfähigkeit von Bindemitteln in Emulsionsfarben

Zusammenfassung

Die Bedeutung der Glasur-Übergangstemperatur (T^g) für die Filmbildung und das weitere Verhalten des Anstrichfilms wird erörtert. Es werden Daten vorgelegt, welche die T^g-Variation bei Kopolymer-Mischung mit ausgewählten Monomerpaaren zeigen.

Witterungseinflüsse verursachen Querverkettung und Abbau der Polymerbindemittel. Während der Witterungseinflüsse vorgenommene Messungen der Veränderungen in den physikalischen Eigenschaften wie Zugfestigkeit, Bruchdehnung, T^g usw., gestatten Voraussagen bezüglich der Dauerhaftigkeit der mit verschiedenen Harzbindemitteln hergestellten Farben im Freien.

*Read before the 5th New Zealand Convention at Wairekei on 11 August 1967 by F. Holland.

Der Verlust an Filmdicke durch Verwitterung kann als Anhaltspunkt für Aufschlüsse über Laugebeständigkeit und Dauerhaftigkeit der Anstriche nach relativ kurzfristigen Witterungseinflüssen dienen.

Die chemische, und im besonderen die Laugebeständigkeit ist in sehr hohem Masse von der Kopolymerzusammensetzung abhängig. Sie lässt sich durch Kurzzeitprüfungen schätzen.

Die Fliesseigenschaften der Farben werden unter besonderer Berücksichtigung der Partikelgrösse der Binde-Emulsion erörtert. Die Auswirkung der Verdickungs- und Verteilungsmittel wird kurz betrachtet.

Расчет связующих веществ и их эксплуатационные качества в эмульсионных красках

Резюме

Обсуждается значение стекло-переходной температуры T_g в образовании пленки и последующее поведение красочных пленок. Прилагаются данные показывающие изменения в T_g по отношению к сополимерному составу в случае подобранных мономерных пар.

Облучение светом приводит к скрещиванию и деградации полимерных крепителей. Измерение вариаций физических свойств как например сопротивления разрыву, критического удлинения, T_g и.т.д. во время обнажения дает возможность предсказать внешнюю прочность красок с различными смольными крепителями. Потеря в толщине пленки во время выветривания может быть использована для получения сведений о сопротивлении против извести и о долговечности красок после сравнительно коротких периодов на открытом воздухе.

Химическое, в особенности щелочное сопротивление зависит в значительной степени от состава сополимеров. Оно может быть оценено посредством ускоренных испытаний.

Обсуждается реология красок в частности по отношению к размеру частиц эмульсии связывающих веществ. Рассматривается кратко влияние сгустителей и рассеивателей.

Introduction

This discussion is restricted to two key features of emulsion design, polymer composition and particle size, and some of their effects on paint performance. To put these matters in perspective it will be convenient first to list the most important requirements that a good emulsion paint has to meet.

Liquid paint

Easy brushing, good levelling, can and colour stability, freeze-thaw stability, good wet-edge and lapping, high build, good tinter acceptance, non-drip, non-sag properties, low temperature film formation, pH stability, rapid drying and most important, low cost.

The paint film

Good adhesion to all surfaces, high outdoor durability, chalk resistance and tint retention, sheen uniformity, high pigment binding capacity, water and alkali resistance, opacity, gloss and gloss retention (for gloss paints), good extensibility, good mar resistance, freedom from burnishing, low dirt retention, easy clean-up and recoatability, non-yellowing.

In the chart below an attempt is made to correlate the paint requirements with polymer properties and particle size. In such a simplified representation some possibly rather too sweeping generalisations must inevitably be made. The items placed between two columns are influenced by the characteristics of both column headings.

A. Polymer characteristics

Soft polymer	Paint properties favoured by choice of monomers	Hard polymer
Extensibility	Alkali resistance	Low dirt retention
Film integration	Water resistance	Mar resistance
Initial gloss		Gloss retention
		Non-burnishing
Exterior durability		Scrub resistance
Colour retention		Easy clean-up
Pigment binding capacity		*Low cost*
Adhesion		

B. Emulsion characteristics

Fine particles	Paint properties favoured by stabiliser system	Medium coarse particles
Pigment binding capacity		Levelling
Opacity		Tinter acceptance
Film integration		Storage stability
Easy brushing		Freeze-thaw stability
Non-sag		Colour stability
Non-drip		High build
Scrub resistance		
Gloss		
Water and water spot resistance		

Polymer design, guided by physical and chemical properties

The glass transition temperature (T_g)

One of the crucial requirements for an emulsion paint is the ability to dry to a completely integrated homogeneous film at the lowest ambient temperatures likely to be encountered. As a prerequisite for this the resin particles in the binder must retain a degree of deformability which allows them to conform to the contours of the pigments and to squeeze into the voids left at even the closest packing of the dispersed particles. The deforming forces responsible for film integration are essentially the surface and interfacial tensions coming into play during and after the drying of the paint. The strongest capillary forces by far appear to be those arising during the drying stage itself, when the continuous water phase escapes from the spaces in between the suspended solids[1]. It is therefore of vital importance that the resin remains deformable during drying and that the rate of water withdrawal—by suction or evaporation—does not outpace the rate of deformation of the resin particles. Otherwise film integration is greatly impaired.

On cooling all polymers become progressively harder and stiffer but remain essentially deformable, viscoelastic "fluids" until, within a narrow, well defined temperature range, they change into glasslike, rather brittle materials which strongly resist deformation. The temperature at which this occurs has been termed the second order or glass transition temperature (T_g) which has many

similarities with the melting point (first order transition temperature) of crystalline solids. At the T_g definite changes occur in the specific heat, modulus of elasticity, thermal expansion coefficient and many other polymer properties. There is also a latent heat of transition similar to the latent heat of crystallisation. T_g determinations may be carried out by a number of different methods, e.g. dilatometry, hardness measurements, determination of torsional modulus or the damping of torsional oscillations, differential thermal analysis, etc.

The results obtained by different methods are usually in fairly good agreement with each other, although some discrepancies have been reported, which can usually be accounted for by different heating or cooling rates and the time allowed for relaxation phenomena.

Since T_g characterises the lowest temperature above which a polymer remains readily deformable it has a considerable bearing on film integration and the minimum film forming temperature (MFT) of the resin emulsion. T_g and with it MFT may be lowered by plasticisers, solvents, and sometimes also emulsion stabilisers. The presence of water, a good plasticiser for polar polymers such as poly(vinyl acetate), poly(ethyl acrylate), etc., tends to depress the T_g so that MFT may be slightly lower than would be expected from measurements carried out on the dry polymer. From the chart it has already been seen that, for a reasonable compromise, a polymer is required which is neither too hard nor too soft, and which has a T_g not too far above the minimum application temperatures. Admittedly some latitude towards higher T_g's is permissible since coalescing solvents, incorporated in the paint, can be used to lower the MFT by perhaps 5-10°C. Generally, however, it will be necessary to have a polymer with a T_g between, say, 15°C and −5°C.

This can be achieved quite readily by the copolymerisation of monomers giving hard or brittle polymers ("hardening" monomers) with those giving soft or flexible polymers ("softening" monomers). Some monomers, e.g. maleic or fumaric esters, do not readily homopolymerise, but are nevertheless able to plasticise or soften a copolymer. The glass transition temperature is one of the most important criteria for the selection of suitable copolymer compositions.

Fig. 1 shows T_g as a function of monomer ratios. Typical hardening monomers are styrene, methyl methacrylate, vinyl chloride, acrylonitrile and vinyl acetate, while softening monomers are exemplified by n-alkyl acrylates, the higher alkyl maleates, fumarates and itaconates, and the vinyl esters of straight chain fatty acids with three or more carbon atoms, "VeoVa" 911 or 10 (vinyl esters of "Versatic" acids 911 or 10).

Above T_g most polymers soften appreciably with increasing temperature, thus accentuating the risk of dirt retention. In most commercially produced emulsions an acceptable compromise has been reached with T_g's between 15°C and freezing point, coalescing solvents being used to ensure film formation down to 0°C or just above.

The glass transition temperature, apart from its close correlation with film formation, is also important in other respects and may affect flaking and crazing. The adhesion of amorphous polymers to smooth substrates, which provide no mechanical key, may suffer a drastic reduction at the T_g while, at the same time, the extensibility is also greatly diminished. Rapid dimensional changes of the

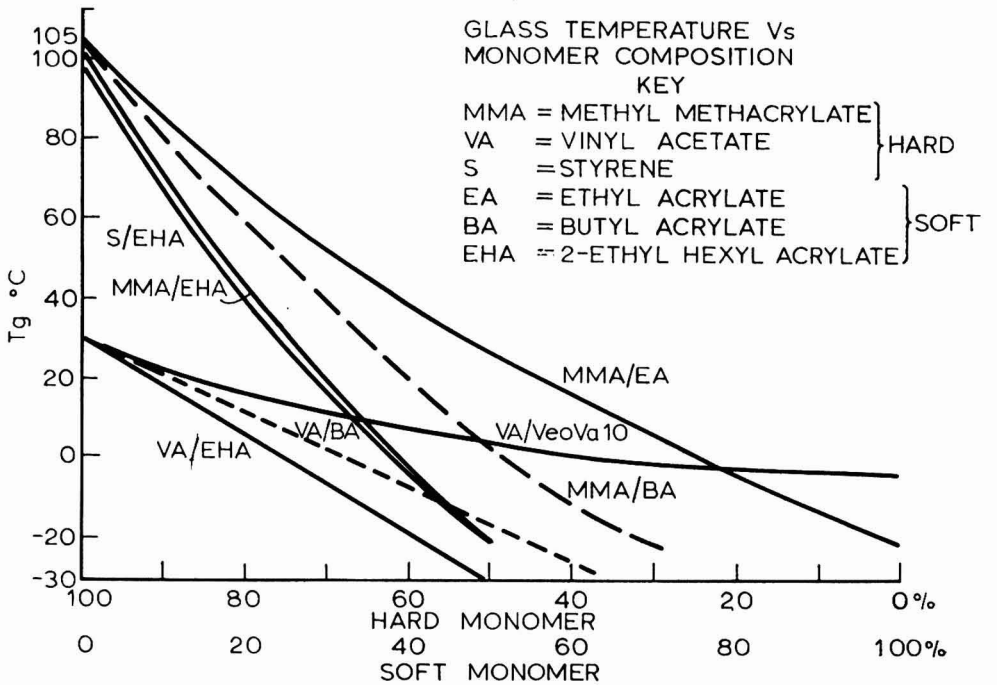


Fig. 1. Relation between gloss temperature and monomer composition

substrate, and, in particular, the formation of ice crystals in or behind the paint film, may then cause its disruption as well as detachment.

The effect of actinic light on the physical properties of paint binders is discussed below. Suffice it here to say that, owing to light-induced cross-linking, the T_g of polymers may be raised by as much as 20 or 30°C. Lightly pigmented systems, e.g. gloss latex paints, which do not filter out the actinic rays so efficiently are sometimes particularly susceptible. An increase in T_g leads to a reduction in dirt retention.

Stress-strain behaviour of resins and paint films

Exterior paint films may suffer considerable stresses in the course of their normal life, either through differential thermal expansion of substrate and paint or more drastically on dimensionally unstable substrates such as wood. Fully satisfactory performance cannot be expected unless the pigmented resin coating can follow dimensional changes of the substrate without rupture. This can only be achieved if the ultimate extensibility exceeds the stretch and if the stress can be relaxed before it exceeds the breaking strength. Both extensibility and stress relaxation are time-dependent. The slower the stretching, the greater the extensibility and stress relaxation.

The study of stress-strain relationships in paint films, giving information on the elasticity modulus, tensile strength and elongation at break, has proved a very useful tool for the prediction of paint performance on exterior exposure. Almost all high polymers undergo considerable changes when subjected to light, heat and rain. The two most important changes are the cross-linking of polymer

chains and their degradation by chain scission. Cross-linking is accompanied by an increase in tensile strength and elasticity modulus (Young's modulus, hardness, stiffness, etc.) and a decrease in extensibility i.e. elongation at break. Chain scission leads to a decay in film strength, softening and, ultimately, the disappearance of the polymer binder from the exposed top layer of the paint film and hence to chalking (see loss of film thickness discussed below).

Unpigmented films undergo these changes quite quickly when exposed to sunlight. They thus lend themselves very well to a rapid evaluation of the photo-chemical stability of polymers. The measurement of physical properties such as stress-strain relationships, tensile strength, elongation at break, polymer solubility and molecular weight as a function of irradiation provides valuable guide lines to the polymer designer who wants to study the effects of monomer choice and copolymer compositions on exterior performance.

In pigmented films, where the resin binder is at least partly shielded from light, similar changes occur more gradually during weathering. The possibility of predicting exterior durability from early changes in physical properties of paint films has been reported by several authors[2]. In a very interesting paper, Schurr, Hay and van Loo have recently been able to demonstrate that paint films whose tensile strength on exposure rapidly reaches a sharp maximum followed by a steep decline will quickly deteriorate through checking and cracking while those showing a slow ascent to a "flat" maximum exhibit good exterior durability.

The correlation between weatherometer ageing, natural exposure and actual performance has been excellent. The screening of new polymers may therefore be undertaken with a fair degree of confidence, under accelerated weathering conditions.

The polymers used in emulsion binders may differ widely in their susceptibility to photochemical cross-linking and depolymerisation. Much will depend on the choice of the hardening and softening monomers and on their relative proportions. The effect of ultra violet radiation on the cross-linking and scissioning of different vinyl and acrylic polymers was studied by Maxim and Kuist[3] whose results indicate that, for instance, poly(ethyl acrylate) depolymerises faster than butyl or ethyl-hexyl acrylate polymers, and that the ratio of depolymerisation to cross-linking per unit dose of radiation decreases with increasing chain length of the alkyl group of the acrylic ester. Poly(methyl methacrylate) requires a 2.5 times higher radiation dose for equal degradation than does poly(vinyl acetate).

The data presented by Maxim and Kuist indicate that ethyl acrylate/methyl methacrylate copolymers will degrade by chain scission appreciably faster than methyl methacrylate/2-ethylhexyl or butyl acrylate copolymers of comparable T_g.

In Fig. 2 the tensile strength of different polymer types is plotted in a semi-quantitive manner against time of exposure, illustrating the different behaviours that may be expected. It has already been mentioned that rapid changes, giving rise to sharp peaks, must be regarded with considerable suspicion. The ascending branch of the curve indicates the hardening or embrittlement of the polymer, while the fall in tensile strength is associated with polymer degradation and breakdown. One is therefore hardly suprised to find that styrene-butadiene

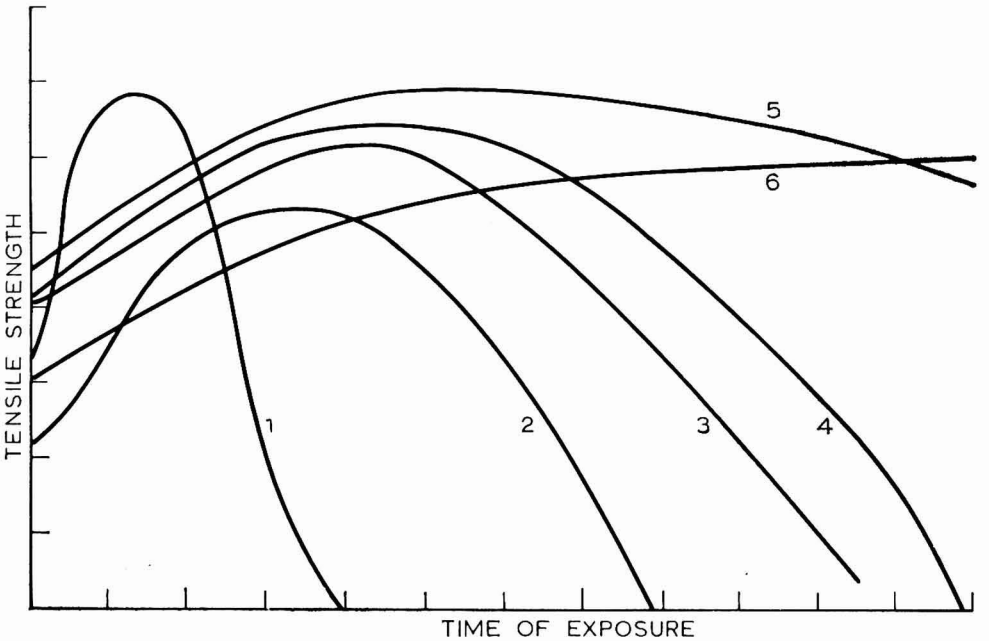


Fig. 2. Changes of tensile strength during exposure

copolymer emulsions, which are known to show poor outdoor durability, have given the results typified by curve 1. Curve 2 shows a somewhat better performance, i.e. that of a medium quality linseed alkyd. Results represented generically by curve 3 are obtained with some vinyl acetate/acrylic copolymers and also with a commercially produced ethyl acrylate/methyl methacrylate copolymer containing a minor amount of a speciality monomer to promote adhesion. These exhibit reasonably good performance, but there is still a suspicion of premature failure through polymer breakdown. Satisfactory behaviour, typified by curve 4, may be found with some styrene acrylic copolymers and also with conventional carboxylated ethyl acrylate/methyl methacrylate copolymers. The best mechanical properties are indicated by curves 5 and 6 such as might be obtained with methyl methacrylate/butyl or octyl acrylate copolymers as well as with vinyl ester polymers containing vinyl esters of highly branched tertiary acids. When designing resin emulsions for exterior paints one should thus pay particular attention to polymers which conform more or less to the tensile behaviour of curves 5 and 6.

The elongation at break declines to a greater or lesser extent during weathering. In Fig. 3, three typical plots such as would be observed with a poor, a good and an excellent polymer are shown. The prolonged retention of high extensibilities is of special importance on dimensionally unstable substrates. Unprimed or emulsion primed wood makes particularly heavy demands on this property. It has been shown for instance that, even on a not too open-grained white pine, paint films must retain an elongation at break of at least 25 per cent (under fairly rapid testing conditions) to prevent cracking. Not many emulsion polymers to date have been found adequate for top coat application on self-primed Pinus Radiata.

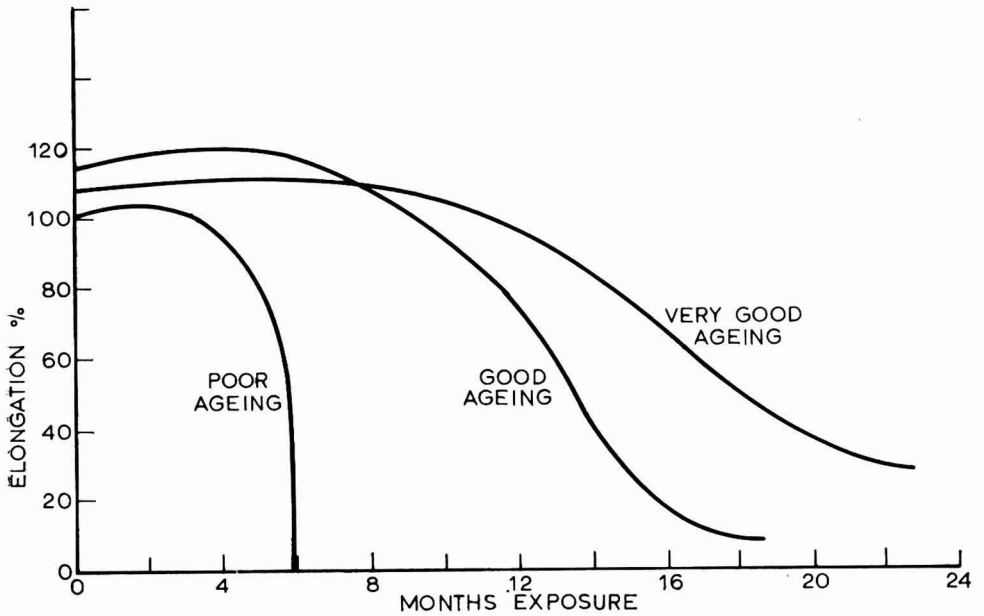
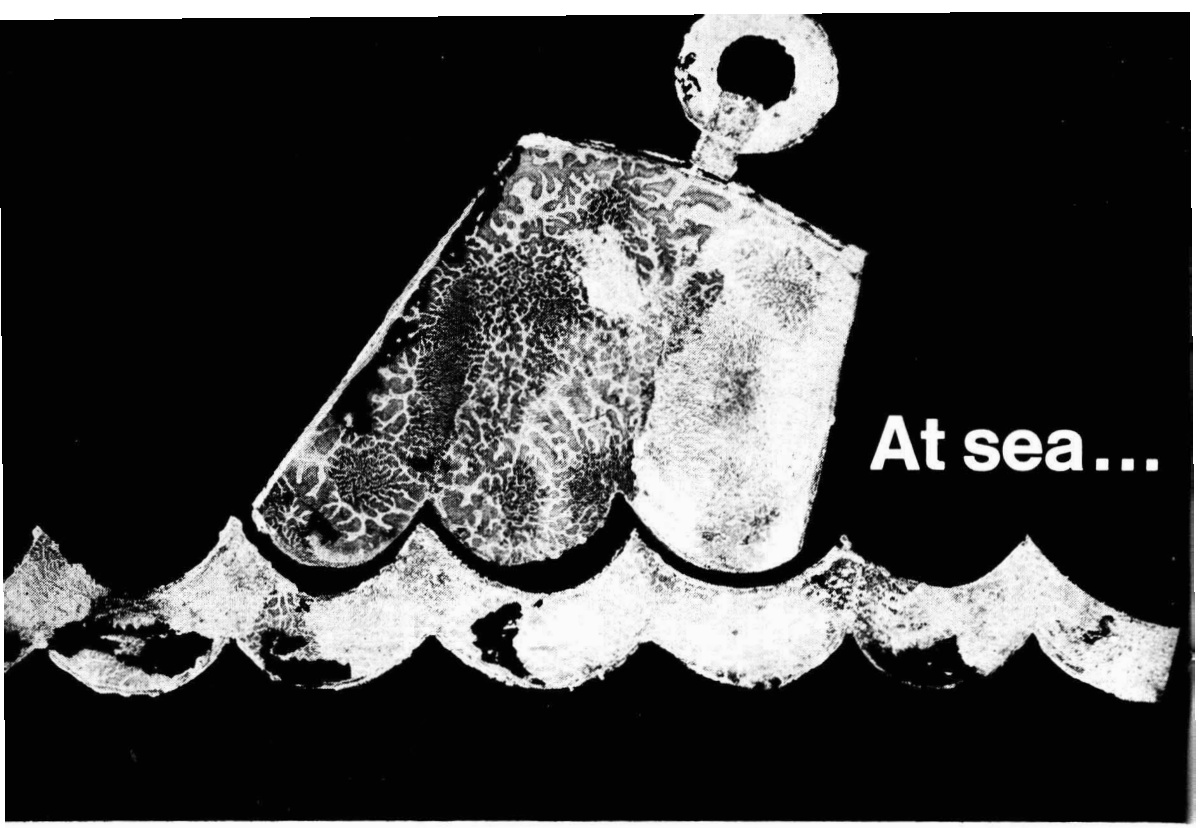


Fig. 3. Elongation at break of paints at 35 per cent PVC

Loss of film thickness

A further test which has yielded interesting and useful advance information on the exterior durability of paint films, measures the loss of film thickness (or weight) during natural or accelerated weathering.

To eliminate substrate effects and to permit accurate weighing, the paint is applied on glass or stainless steel panels. It is then dried for 24 hours in the laboratory, preferably leached in distilled or rain water for the removal of water solubles, dried to constant weight at controlled temperature and humidity, e.g. 20°C, 75 per cent RH and finally placed on a test fence, facing the mid-day sun. The angle may be chosen according to the information required but is usually 45°. At intervals of 4-6 weeks the test panels are taken from the exposure rack, very gently swabbed with a weak detergent solution to remove adherent dust and dirt, rinsed and re-dried at constant temperature and humidity. The weight or thickness loss due to exposure is recorded and plotted against time. The errors arising out of dirt retention are almost negligible. Figs. 4 and 5 show in typical plots how different polymers differ widely in their rate of erosion under the influence of natural weathering. Paints in graph 4 were made to 40 per cent PVC and in graph 5 to 50 per cent PVC. At 50 per cent PVC the loss of film thickness is 1.5-2.5 times greater than at 40 per cent PVC over a comparable period. It is also worth noting that attrition rates settle down fairly quickly so that, allowing for seasonal variations, the slope of the curves may be used at a fairly early date for durability predictions and hence polymer evaluations. The correlation between erosion rates and exterior durability, especially chalking, has on the whole been very good. Different orders of relative merit are sometimes established for the polymers when they are tested under different climatic conditions. This is hardly surprising, since



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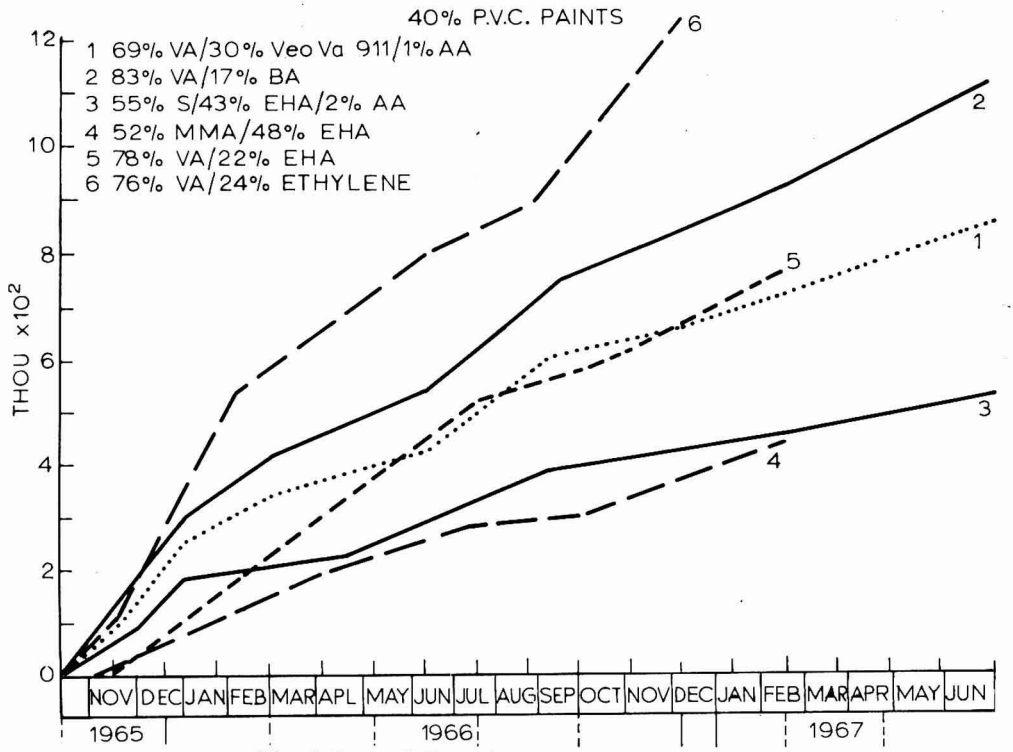

Fig. 4. Loss of film thickness during exposure

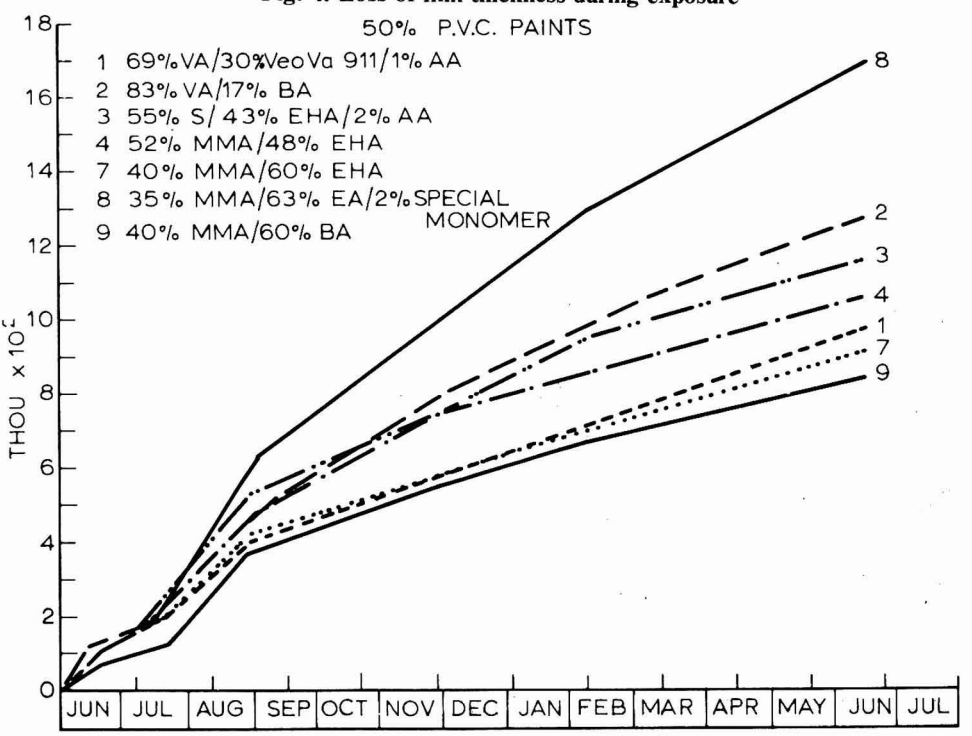

Fig. 5. Loss of film thickness during exposure

the interplay of destructive agencies such as UV light, rain, frost, etc., differ from place to place. By comparing stress-strain behaviour, erosion data, changes in glass transition temperatures, etc., during outdoor exposure, the resin manufacturer is greatly helped in choosing the right polymers for each geographical area. The graphs shown here refer to experiments carried out in the UK. Similar results, with some minor variations, were obtained in Durban (South Africa).

Alkali resistance and efflorescence

Emulsion paint films may be subjected to severe chemical attack, especially from strongly alkaline cement, asbestos cement or plaster substrates. The efflorescence of water soluble salts may present an additional problem. It should be remembered in this context that the two phenomena often described as "lime burning" and "lime blooming," though related to each other, are caused by two rather different mechanisms. Lime burning may be ascribed directly to the hydrolytic destruction of a saponifiable binder, while lime blooming and similar efflorescence effects are caused by water soluble substances migrating through or out of the paint film to the surface. Water solubles inclined to bloom out are usually electrolytes, especially metal carbonates, hydroxides and sulphates, which crystallise as hydrates. To provide favourable conditions for efflorescence, the paint film must be able to absorb or contain sufficient moisture to dissolve the offending substances. Alternatively, it must be porous, i.e. pigmented to a volume concentration above CPVC. After initial drying and coalescence, the paint film will be susceptible to efflorescence more or less in proportion to its water up-take, which is influenced by the water solubles and the polymer itself. Hydrophobic binders, such as styrene-acrylic copolymers, can give films which remain virtually free from any surface bloom, while the relatively hydrophilic vinyl acetate-acrylic copolymer paints are much more prone to disfiguration. The bloom is often removed again by rain water (and carbon dioxide), but occasionally white crystals remain embedded in or near the surface, where they can give tints a blotchy appearance. Pure acrylics, e.g. methyl methacrylate/acrylic ester copolymers, are fairly free from efflorescence problems especially if they are based on the more hydrophobic higher alkyl acrylates. The same is true for copolymers of vinyl acetate containing a major proportion of long chain vinyl esters, especially vinyl esters of tertiary, highly branched carboxylic acids. Good adhesion to efflorescing substrates helps to prevent crystal growth behind the paint film. There appears to be a high correlation between alkali resistance and freedom from blooming.

Completely alkali resistant paint films can only be obtained with polymers that themselves are immune to alkaline saponification. Copolymers containing substantial proportions of styrene, vinyl chloride, methyl methacrylate, a tertiary alkyl acrylate or a vinyl ester of a carboxylic acid with a fully substituted α carbon atom, are very alkali resistant. Copolymer compositions aiming at high alkali resistance, therefore, usually contain one or more of these monomers.

Two simple screening tests for "lime burning" and "lime blooming" may be carried out by the emulsion designer.

(1) A tinted paint is applied to a previously self-primed sheet of asbestos cement and allowed to dry for 24 hours. The sheet is laid, paint side upwards, on to a slab of cellular, e.g. polyurethane, sponge which is immersed to within approximately $\frac{1}{8}$in from its top surface in a bath consisting of sea water (natural or synthetic) saturated with calcium sulphate and calcium hydroxide. The paint surface is exposed to heat, e.g. the sun, or infra-red lamps placed 3-4ft above the panel, for eight hours a day and then wetted with water by means of a fine spray. The edges of the panel are preferably smeared with vaseline or silicone grease to minimise salt creep. The paint is examined for efflorescence and signs of deterioration after various periods.

(2) Detached paint or binder films of controlled thickness and known weight are immersed in saturated calcium hydroxide solutions, contained in sealed jars. The jars are placed in a thermostat or oven at 30°C. The loss of film weight is determined at intervals for a total period of 2-4 weeks. The films are first freed from adhering solutions by rinsing or dabbing and then dried to constant weight.

Pigment binding capacity

Pigment binding capacity means different things to different people. It may therefore be fruitful to look at the most important factors involved.

CPVC

The critical pigment volume concentration (CPVC), i.e. the maximum volume fraction of a pigment or extender which can be accommodated in a paint film without the formation of voids, is a function of both the pigment and the binder emulsion. It is not proposed here to discuss the effects of pigment size, shape and packing but to consider only the role of the binder. The CPVC of a paint system may be determined experimentally in a number of different ways. The methods most commonly employed measure the tensile strength, conductivity, density, permeability or enamel hold-out of the paint film at different pigment binder ratios. When the measured properties are plotted against PVC a well defined discontinuity is apparent at the CPVC (see Fig. 6).

Factors affecting CPVC

How is the CPVC likely to be affected by the properties of the emulsion and the polymer? Three factors must be of significance: the particle size, the deformability of the polymer and the ability of the paint system to maintain a high degree of deflocculation until the pigment is wetted by the binder resin. From purely mechanistic models (see Fig. 7) one can predict that emulsions will have a high pigment binding capacity in terms of high CPVC if:

(1) the polymer is readily deformable.

(2) the emulsion particles are fine.

(3) the pigment remains well deflocculated in the paint film.

Condition (1) requires a soft polymer with a low T_g. With regard to condition (2) Becker and Howell have shown that the CPVC of a polyvinyl acetate

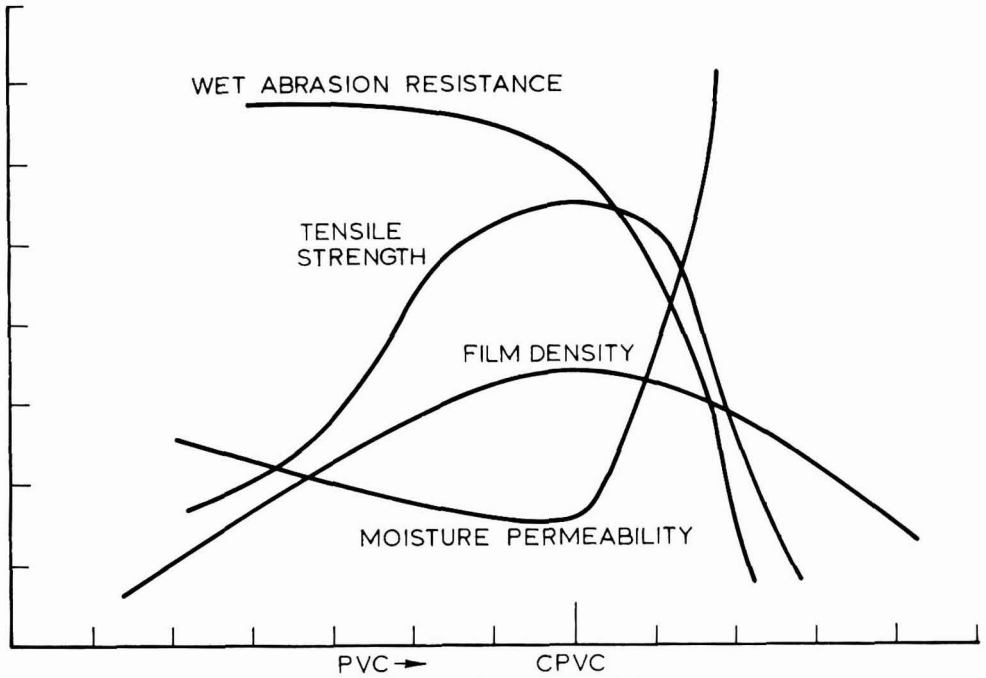

Fig. 6. Change of properties with PVC

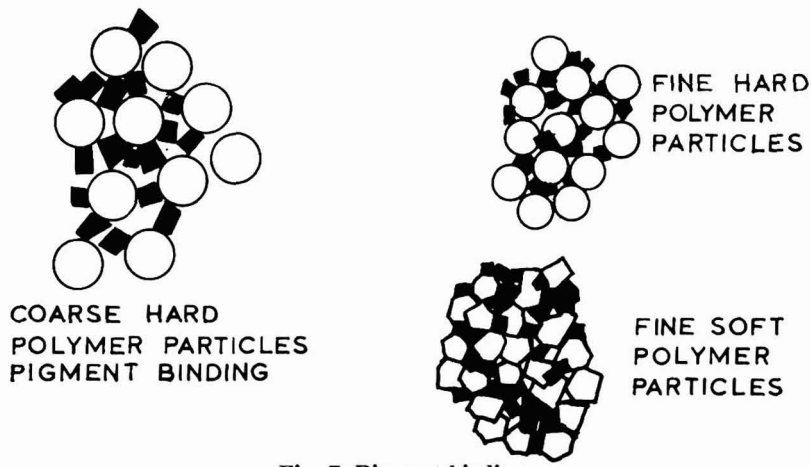

Fig. 7. Pigment binding

emulsion rose from about 42 per cent with particles of 1 micron diameter to about 49 per cent when the particle size was reduced to 0.2 microns[5]. Their results may be represented in good approximation by the equation

$$\text{CPVC} = 10 \times (4 - \log \text{particle size in microns}).$$

The desirability of maintaining a high degree of deflocculation of the pigments until they are wetted by, or at least adhering to, the binder resin is almost self-evident. Particles not able to make intimate contact with the binder are, by definition, badly bound.

Many paint chemists would judge pigment binding capacity by rather different criteria. They may be particularly concerned with scrub resistance, ease of removal of surface pigment or the maximum permissible pigment loading for exterior paints.

While the considerations outlined above give the emulsion manufacturer some important guide lines on pigment binding capacity, very often more complex factors like pigment flotation, flooding or co-precipitation may also enter into the picture. These factors may be more under the control of the paint maker than the polymeriser. Scrub or wet abrasion resistance is not exactly a simple phenomenon but it ties in fairly well with CPVC, as was shown by Liberti and Pierrehumbert[6] who demonstrated the rapid decline of scrub resistance above CPVC. A comparison between different emulsions of equal pigment loading additionally focuses attention on the water sensitivity of the emulsion system and the ingredients used in the mill base, notably the thickeners and dispersants. Last, but not least, the water up-take of the polymer is a significant factor. It has been fairly generally observed that at equal particle size, hydrophobic resins, e.g. styrene-acrylic copolymers, have a higher pigment binding capacity in terms of scrub-resistance than the more hydrophilic copolymers of vinyl acetate and acrylic, maleic or fumaric esters.

Rheology of the liquid paint

The properties of the paint film discussed so far were found to be determined predominantly by the polymer itself. Attention may now be turned to the liquid paint and in particular its rheological behaviour. This is largely determined by the emulsion characteristics and more specifically by the particle size and size distribution of the dispersed resin phase. The mill base ingredients and the method of paint manufacture are, of course, equally important.

The rheological characteristics of greatest interest are those controlling brushability, levelling, sagging and dripping. While it is difficult to correlate rheological properties of emulsion paints unequivocally with emulsion or mill base parameters, some general observations may be made and specific cases examined.

Levelling

The levelling of emulsion paints is a very complex phenomenon, which has acquired special significance in latex gloss paints. Two inter-related aspects must be considered: the *rate* and the ultimate *extent* of flow-out.

The levelling rate is inversely proportional to the viscosity (η) of the paint after shearing under the brush: $2LR/\eta$. The extent of levelling is determined by the equilibrium between the forces striving to promote and to oppose the restoration of a level surface. The predominant restoring force is surface tension—with gravity playing only a negligible part—while the opposing force is the yield value (structure, body) of the paint. The simplest way of expressing this equilibrium is by the equation $r=2\sigma/Y$ where "r" represents the radius of curvature (in cm) of the ridges remaining when flow-out ceases, σ the surface tension in dyne cm^{-1} and Y the yield value (in dyne cm^{-2}). The surface tension of practical emulsion paints is usually of the order of 30-45 dyne cm^{-1} and cannot be raised much beyond this range without an adverse effect on substrate wetting, pigment dispersion and storage stability. The condition $r=\infty$ is, of

course, that of a perfectly level surface. Expressions linking surface tension and yield value with the height of ridges remaining after the cessation of flow-out have also been derived but they are rather more complicated and the literature should be consulted for details[7].

This looks very straightforward so far since all one needs to ensure for good levelling is that, after shearing, both viscosity and yield value of the emulsion paint should be low. There is no unsurmountable obstacle there; the difficulties arise out of the fact that viscosity as well as yield value rise quickly with time. Three factors are chiefly responsible for this, i.e. the thixotropy of the paint, evaporation at the surface and loss of water by wicking into porous or absorbent substrates.

Thixotropy

The paint is thixotropic, i.e. its viscosity and yield value (structure) are reduced by shear but recover at rest. Brushing, at shear rates of approximately 10^4 sec^{-1}, lowers both η and Y almost to their limiting minimum values. As soon as the brush is removed recovery begins. Both quantities are measurable on a variable shear viscometer.

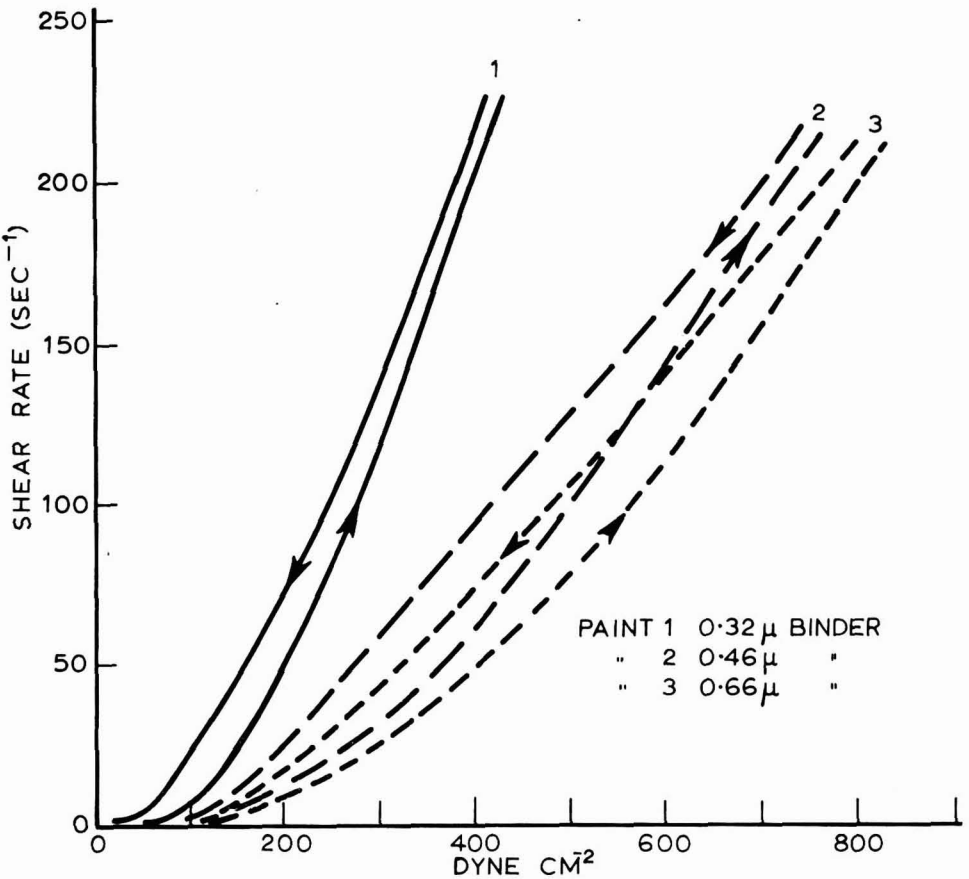

Fig. 8. Rheology of acrylic semi-gloss paints at 55 per cent TSC

The author has measured the viscosity as a function of shear rate on three paints compounded to the same formula and using three emulsions of identical composition but varying particle size. The emulsions were of the all-acrylic type and colloid stabilised; the paints, formulated for semi-gloss, were made to a PVC of 24 per cent and a solids content of 55 per cent. The results are shown in Fig. 8 as stress/strain plots. Unfortunately the viscometer used does not span a very wide range of shear rates, but even so a fairly clear picture emerges. The finer the particle size the faster the viscosity recovers after shearing. This is indicated by the area of the hysteresis loop between the "up" and "down" curves, where the viscosities were measured at ascending and descending shear rates. Note the wide separation in the paint with the coarsest emulsion. From this it may be concluded that levelling is favoured by coarse, and impaired by fine, particles.

Similar effects of particle size on yield values have been observed by Kreider[8] who examined styrene-butadiene emulsions of varying particle size and measured the recovery of yield value after agitation in a high-shear food liquidiser.

In seeking an explanation of the observed phenomena the following points must be considered:

(1) At equal concentration the average "stand-off" distance between the suspended particles decreases with decreasing particle size. See Fig. 9 which represents diagrammatically the cross-section of a suspension containing equal volume concentrations of particles of 0.5 micron and 0.25 micron diameter respectively. It must be remembered that for every

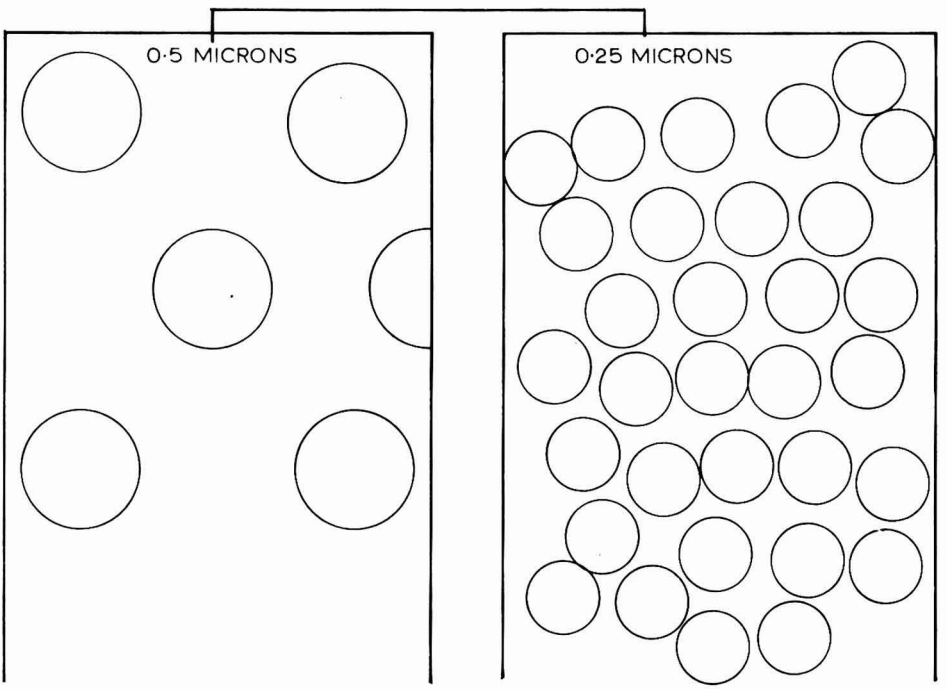

Fig. 9. Cross-section of dispersions of equal concentration

0.5 micron particle eight 0.25 micron particles have to be accommodated in the same space.

(2) The total surface area presented by the disperse phase increases in inverse proportion to the particle diameter.

(3) Thickener molecules may be adsorbed by the particles, if at the interface there are any unoccupied sites available to which they can become attached. The chance of this being the case is much greater in systems with large internal surface areas, namely fine particled ones.

(4) Simultaneous adsorption of thickener molecules by two or more particles may lead to bridging and the formation of a network structure. The strength of this structure (yield value) will depend on the number of links that can be formed.

(5) Particle bridging by thickener molecules, and hence the formation of network structures requires (a) the presence of sufficient latch-on points at the particle surfaces and (b) molecules long enough to span interparticle distances.

If levelling were the only concern in binder design or paint formulation a simple set of rules could be followed:

(1) Avoid emulsions or extenders of too low a particle size, say below about 0.5 microns.

(2) Choose thickeners of sufficiently low molecular weight to ensure that the thickener molecules—in their configuration in aqueous solution—are too short to span the inter-particle distances.

(3) Saturate the surface of all dispersed particles, e.g. with surfactants, anionic dispersants or low molecular weight colloids before adding the thickener, to eliminate unoccupied sites. Alternatively, use sufficient thickener to obviate the need for two particles to share one colloid molecule.

The effect of thickener concentration on yield values of paints was studied by Garrett, Prentiss and Scott[9] whose findings, recorded in Fig. 10, clearly demonstrate that an increase in thickener concentration from 1 per cent to 4 per cent lowers the yield value almost to vanishing point.

It has been stated in the literature[9] that water loss through drying cannot influence viscosity and yield value to any great extent during the period normally required for levelling, i.e. 2-5 minutes. This conclusion was reached when the overall weight loss of wet paint films, during the first five minutes of drying, was found to be too small to account for a significant increase in total solids content. The validity of this argument is questionable. An increase in concentration, and hence viscosity and yield value at the paint *surface* matters far more than a mere overall water loss from the film as a whole. A "skin" of highly viscous or structured paint would almost certainly inhibit levelling under the influence of surface tension. The existence of a concentrated surface layer and a concentration gradient across the thickness of the film may be postulated simply from diffusion laws.

Unfortunately it is not yet possible to measure solids content, viscosity or yield value at the surface of drying paint films, but even simple weight loss

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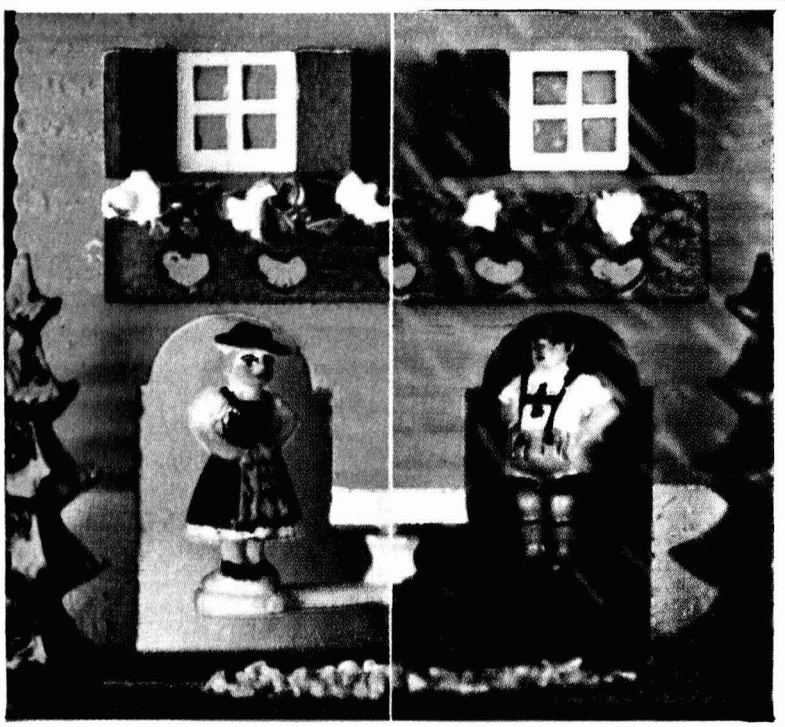

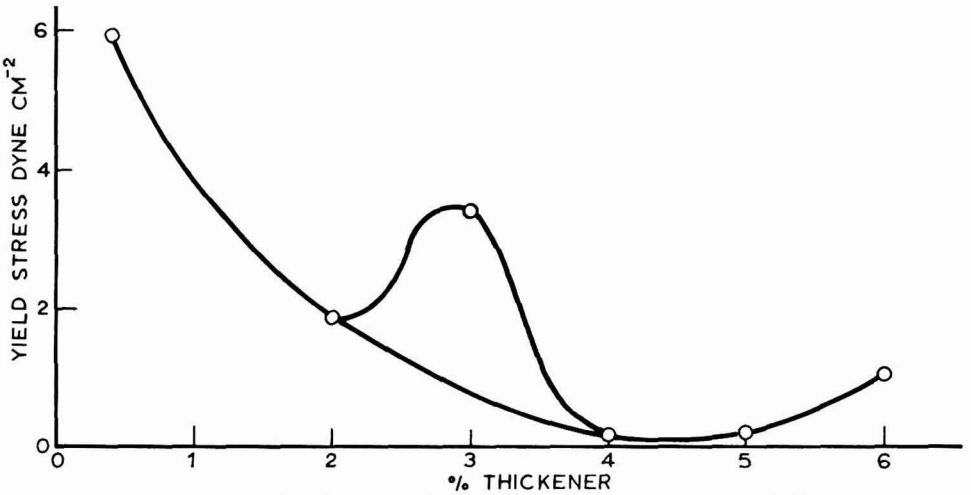

Fig. 10. Relation between yield stress and volume per cent thickener

determinations may give useful information on the rate of moisture release from the surface and its control by specific binder or mill base ingredients. There may also be a particle size effect, but this has not yet been firmly established. Wet edge control is clearly a closely related problem.

Wicking

On certain substrates the abstraction of aqueous dispersion medium by wicking may become the major factor affecting the rate and extent of levelling[9]. Paints with good levelling characteristics should therefore preferably be designed to have low wicking rates. In the absence of sufficient basic information, this may still have to be done largely by trial and error. Certain guide lines can, however, be laid down: low wicking rates are favoured by a high viscosity of the aqueous phases, a high degree of deflocculation and stability in the paint system, by fine particles, by avoiding pigments and extenders which could act as "filter aids" like diatomaceous silica and by a high contact angle of wetting at the paint/substrate interface (a rather hypothetical condition, excluded by the need for good substrate wetting).

Wicking rates, while not easily predictable, may be estimated with very simple equipment[9]. One end of a strip of a coarse filter or chromatographic paper is dipped into the paint sample, contained in a conical flask. The flask is then sealed with a rubber stopper which also serves to hold the dry end of the strip in position. The strips are examined after a set time, say two hours. The height to which clear water phase has risen in the paper is a measure of wicking rate. Fine particled emulsions and pigments tend to give a dense "filter cake" and/or clog the capillaries and thus reduce wicking. A similar effect is observed where oils, e.g. drying oils or low molecular weight alkyds, have been emulsified in the emulsion.

Brushability

The ease with which a paint can be spread depends on its viscosity at brushing shear rates (10^4 sec^{-1}). Newtonian liquids whose viscosity remains constant over

the entire shear range give a lot of brushing drag and feel sticky at viscosities as low as 5-6 poise, whereas thixotropic emulsion paints with viscosities exceeding many times that value at rest, have a soft silky feel under the brush. Since brushability is largely a function of the viscosity breakdown with shear, it is favoured by fine particled emulsions which give more shear dependent paint viscosities than coarse emulsions.

Since the best levelling characteristics are found with near-Newtonian liquids, there is almost invariably conflict between the paint requirements for easy application on the one hand and good levelling on the other. Only a, sometimes rather uneasy, compromise can resolve this particular problem. The simple way out, namely a reduction of solids content, can rarely be tolerated, because opacity and build would suffer and sagging become a real danger.

Sagging

With emulsion paints this has not often caused any major difficulties. The gravitional pull on relatively thin films is not normally strong enough to overcome the rising yield value and viscosity. Nevertheless, it is obvious that sag resistance and good levelling are incompatible. Consequently, the easiest way to obtain paints that do not sag is to use fine particled emulsions and pigments.

In thick films, where the shear stress due to gravity may be larger than the yield value, the top layer will sag at a rate which is proportional to the square of film thickness and inversely proportional to viscosity. Single coat high build finishes can, therefore, only be formulated by sacrificing levelling almost entirely. For that reason they are usually deliberately textured. While, in normal film thicknesses, fine particled binders would be the obvious choice for highly sag-resistant paints, they are not particularly suitable for high build compositions. To avoid crazing in thick coats, especially in blow holes, it is necessary to work at rather high solids contents. Fine particled emulsions do not lend themselves too well for that, and aggravate the crazing or star cracking tendencies so frequently observed in very thick emulsion paint films on drying. Sagging must therefore be controlled by suitable thickeners which ensure an almost instantaneous recovery of structure and viscosity after shearing.

Dripping

Drip-free paints should have a high viscosity and/or structure when at rest in the can. Their viscosity should not be broken down too readily at low shear rates (brush insertion or transport) and should preferably recover quickly after shearing. Again, fine particled emulsion binders are indicated, so that a really drip-free paint may be difficult to formulate with good levelling characteristics. By the use of medium-fine to coarse particled emulsions and the inclusion of gelling agents like zirconium or titanium compounds a reasonable compromise may be reached.

[*Received 31 January 1968*

introduction to paint technology

second edition with additional chapter

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

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

new chapter

The new chapter is subdivided to three sections

resins and media

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

application techniques

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

instrumental testing and control methods

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

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

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International sponsored research*

By D. S. Newton

Imperial Smelting Corporation (Alloys) Ltd., Bristol

Summary

The origins, history and organisation of the International Lead Zinc Research Organisation Inc. are described, and mention is made of some of the research programmes which are of interest to the surface coating industry.

Recherches soutenues internationales

Résumé

On décrit les origines, l'histoire et organisation de la International Lead Zinc Research Organisation Inc., et l'on mentionne quelques programmes de recherches qui intéressent l'industrie de revêtements superficiels.

International Unterstützte Forschung

Zusammenfassung

Die Ursprünge, Geschichte und Organisation der International Lead Zinc Research Organisation Inc. werden beschrieben, und einige Forschungsprogramme, die für die Oberflächenbehandlungs-Industrie von Interesse sind, finden Erwähnung.

Международно утвержденные научные исследования

Резюме

Описываются происхождение, история и организация «Объединенной Международной Организации по Исследованию Свинца п Цинка» и упоминаются некоторые программы научно-исследовательских работ которые представляют интерес для промышленности поверхностных покрытий.

The fact that industry research associations not only exist, but expand at a time when individual companies' own research efforts are increasing, appears at first sight to be an anomaly. The question can be posed as to whether a company is not the best judge of how to invest in research carried out under its control, so having the benefits of secrecy and its subsequent financial advantages, rather than providing an income to independent organisations (probably from its own research budget), and having no prior claim on the information produced by them. The history, organisation and present status of the International Lead Zinc Research Organisation Inc. of New York may well go some way towards demonstrating their place in industrial society.

Like England, the USA has very active promotional organisations for zinc and lead, namely the American Zinc Institute and the Lead Industries Association (AZI - LIA), and it was in 1957 that the executive heads of these two bodies, together with senior members of five of the major lead and zinc producers,

*Chairman's Address to the Bristol Section on 29 September 1967.

studied the feasibility of forming a co-operative research organisation. The reasons behind this move were simple; both the lead and zinc industries throughout the world spent less on research as a percentage of income than did the competitive industries, even though the potential usefulness of both metals and their derivatives had never been fully exploited. Thus the market for both was in certain areas at risk, and their public images almost non-existent. From the activities of this small group of people developed the AZI - LIA Expanded Research Programme, with an original membership of 19 producing companies located in Australia, Canada, Mexico, England and the United States. The method of operation was kept as simple as possible, contracts being placed with suitable research laboratories for specific projects, and being paid for out of income derived from an assessment on each ton of metal produced. Progress reports on the work in hand were published at regular intervals and made available to the member companies and consuming industries. The work in progress, the administrative organisation, and profitable areas of research were in the hands of an executive committee and technical steering committees.

In 1958 Dr S. F. Radtke left the aluminium industry to become Director of Research and he built up a team of metallurgists, chemists, economists and development engineers whose duties were to manage work in progress and to act as liaison officers between the research contractor and the members. Committees were set up on a wider basis, comprising representatives of member companies whose terms of reference were to suggest new programmes and to discuss the progress of those already active. Some form of classification was obviously necessary, and there developed chemical, electrochemical and metallurgical committees for both lead and zinc, to be followed later by an environmental health committee for lead.

1959 saw the organisation of the distribution of ERP Research Digest through American and British development associations and members, which was later followed by the printing of the same material in other languages, and distribution by various other national lead and zinc promotional organisations.

Membership expanded, the first member in Continental Europe being Montepone and Monteveccio in Italy in 1961. The two Japanese producers Mitsui Mining and Smelting Co. and Mitsubishi Metal Mining Co. joined in 1963 and 1966 respectively.

In 1963 the Expanded Research programme was renamed The International Lead Zinc Research Organisation, abbreviated to ILZRO, in order more correctly to describe its activities. The final change to incorporate it as an independent body under the laws of New York City took place in 1965 with 26 companies as Charter Members.

That in brief gives the history of the Organisation; the more detailed reasons behind its origins can be given in three statements:

1. There is a world wide large capital investment in both lead and zinc in terms of mines, concentrators and plant.
2. With both metals the major applications are limited but of very high tonnage.
3. With technological advances in other materials, certain of the traditional markets for these metals are at risk.

A few examples for each metal may be cited. The lead acid SLI battery at present has no obvious competitor, but with the present rate of the advances in technology its position cannot be regarded as impregnable. Lead cable sheathing is another outlet at risk, its market having been drastically curtailed by the increased use of polyethylene where the latter's low specific gravity gives it a tremendous advantage. In the zinc applications field the two largest outlets are in hot-dip galvanising and pressure diecasting. The former can be replaced in some cases by aluminised steel, pvc coated steel or weathering steels, whilst the latter is vulnerable to some of the more recently developed thermoplastics. Research is necessary to combat these attacks and the possible loss of markets.

Against this, however, is the fact that some areas of lead and zinc technology are virtually undeveloped, and many unexplored, with the possibility that highly profitable returns are being missed. The situation is by no means confined to lead and zinc, however, since every material produced is vulnerable to some degree from the moment its properties, applications and economics are known. Taking these points into consideration, the evolution of the strategy of research by ILZRO becomes clear. There are four main areas in which research can usefully be activated.

1. *Defensive.* To improve present products and to make them more competitive. To obtain objective information on zinc and lead products, thus identifying their advantages and shortcomings.
2. *Offensive.* To develop new products or processes which can introduce lead or zinc into markets already held by other materials.
3. *Development.* To provide new materials via fundamental research which will create new markets.
4. *Humanistic.* To collect and disseminate information in areas where it will be most beneficial.

Suggestions for programmes of work do not arise entirely from the committees previously mentioned. Any organisation, commercial or educational, can forward a proposal, which should include a description of the work to be done together with costs. Subjects arising from the committees are circulated to organisations known to be interested in particular subjects suggested, and a proposal for the work is invited. The principles governing the acceptance of a proposal depend on a number of factors which are really more detailed versions of the above four philosophies.

1. New or improved products or processes.
2. Opening new markets or potential marketability.
3. Reflect the advantages of co-operative research in all its aspects versus individual company work.
4. Involve customer participation.
5. Add to the technical and economic knowledge within the fields of lead and zinc.
6. Help to build an image of lead and zinc and their compounds as modern versatile materials.

This last comment may seem rather odd, but there is a tendency to assume that because both lead and zinc have been known for centuries, and their major

outlets are few but well defined, there is little fresh information to be gained, and that gaining it will be of little profit.

Other important aspects of the research work undertaken in which ILZRO is involved are:

1. Systems engineering for products and processes.
2. Cost centre analysis for key operations.
3. PAP—Price, Availability and Performance analysis and customer reaction.

Systems engineering involves the complete analysis of a product from idea to full commercial exploitation, and includes all those steps in manufacture which are critical in the overall performance of the product.

Cost centre analysis identifies those critical operations in a manufacturing process which must be improved or eliminated if a product is to remain competitive.

Price, availability and performance analysis is effective in meeting competition, and has for instance enabled organo-lead compounds to be competitive with organo-tin compounds in many applications.

Customer participation is invaluable for introducing new products or processes; it enables a product or a process to be objectively evaluated and compared with current materials or practices, and also indicates the most profitable direction for further research. Lectures and symposia fall into this category, and many have been held, particularly on subjects such as plating and storage batteries. The evaluation of new products by users has given a tremendous amount of information, and has on many occasions pointed out completely new areas of research.

Allocation of research programmes

In geographic terms the majority of the research contracts are held by companies, research associations and universities in the United States and Canada, but during the last few years, with the increasing awareness of ILZRO throughout the world, many applications for funds to carry out work are coming from elsewhere. Programmes of research are active in Germany, Holland, Italy, Japan, Australia and the United Kingdom.

Well-known organisations which have been or are so engaged are the TNO at Utrecht (Organo-metallic compounds) Max Planck Institute at Stuttgart (Zinc alloys), BNFMRA (Surface characteristics of zinc and diecasting alloys and plating processes), British Welding Research Organisation (Welding of zinc coated steel), Paint Research Station (Hazing of paints containing zinc oxide and the painting of zinc sprayed steel) and the University College of North Wales at Bangor (Zinc and copper tolerances in plants and micro organisms). Professor Douglas at Sheffield has completed a study of the physical and chemical properties of zinc oxide in glasses, whilst the Yarsley laboratories have investigated the litharge/glycerol cement analogues. The General Electric Co. have a contract to investigate the manufacture of zinc tubing.

Other non-American contracts are held by the University of British Columbia, Electrolytic Zinc Company of Australasia, British Columbia Research Council, Tokyo Institute of Technology, Centro Ricerche Metallurgiche SpA, Turin,

Centro Nacional de Investigaciones Metallurgices, Cuidad University, Spain, Canadian Department of Mines, University of Melbourne and the University of Queensland.

Research programmes

To date, roughly 250 programmes have been sponsored, divided about equally between lead and zinc. The lead programmes completed deal with lead in ceramics and glass, plating, and fatigue cracking, whilst a second series describe work on its acoustic uses, continuous sheet casting, and the screening of organo-lead compounds for endocrinological and antimammary tumour activity.

Metallurgical research in progress covers a wide field, and includes architectural applications, wrought lead, cable sheathing, solders, jointing, cladding of steel, battery applications, corrosion control, and fundamental investigations into fatigue strength, powder metallurgy, alloy properties and surface reactions. Lead chemistry includes the synthesis of organo-lead compounds, and their efficiency as anti-fouling compounds, rot-proofing agents and wood preservatives. The properties of lead pigments in water-thinnable media and in electrodeposited finishes are also being investigated. The use of lead chemicals in ceramics, an old established use, is being actively examined, as is their application in the allied fields of porcelain enamels and glasses.

In the zinc sector much of the completed work deals with aspects of die-casting, hot dip galvanising and the properties of zinc alloys. The development of improved zinc litho plates has also been carried out, and the results published: 280,000 impressions on a four-colour machine were successfully obtained with no distortion of the plates. Information is also available on zinc shot blasting, zinc in nutrition, zinc pigments in water-thinnable coatings and the powder cladding of steel.

Current programmes include an investigation into clear finishes for zinc, chromium plating, gravity casting alloys, the effect of zinc surface conditions on painting, organo-zinc compounds, electrophoretic deposition of paints containing zinc pigments, and zinc dust paints. Epoxide polymerisation by organo-zinc compounds is also under active investigation. Obviously, many of these programmes, whilst interesting in themselves, do not have any bearing on the surface coating, printing or ink industries; but there are some which merit a more detailed treatment, particularly in the field of zinc.

Zinc pigments and the painting of zinc

a. *Zinc pigments in electrophoretic deposition systems (ZC89). Eagle-Picher Industries, Joplin, Missouri:* This programme is a good example of the co-operative nature of ILZRO work, in that Imperial Smelting Corporation Ltd. was able to put Eagle Picher in touch with UK resin and pigment companies with interests in this field. Compatibility has been a problem in some cases, but some promising results have been obtained with UK produced zinc orthophosphate.

The electrodeposition of zinc dust primers based on latex binders which are claimed to deposit on the cathode has been examined. The problem to be overcome is the control of the relative rates of deposition of the pigment and the latex, that of the latter being several times greater than that of the zinc dust.

b. *Evaluation of zinc surface conditions on painting* (*ZC65*). *Eagle-Picher Industries:* Those who are directly concerned with industrial surface coatings will be well aware of the problems which can occur when painting hot dipped galvanised steel. In the USA the problem is even more complex due to the fact that there are many more galvanising lines and a greater variety of passivation treatments to prevent "wet storage stain." Since most GS is sold through stockholders, it is not unusual for one consignment to a customer to contain sheet from more than one producer.

The programme consists of an examination of the exterior durability of conventional American paints on galvanised sheet supplied by each major producer, and attempts to relate this performance to the type of zinc surface and the type of pretreatment if known. Since many of these pretreatment systems are proprietary in character, some difficulties obviously arise, but it is hoped that sufficient information will be available in due course to provide an information booklet on the subject.

c. *Fundamental study of paint adhesion to zinc* (*ZE94*). *Battelle Memorial Institute, Columbus, Ohio:* This programme, closely allied to the previous one, is investigating the metallurgy of galvanised surfaces, with the intention of correlating variables present with paint failure. The effect of passivating treatments on paint adhesion to various types of galvanised coating is also included. The work done so far has been concerned with the impurity level in the zinc surface, and the absence of alloying materials in the zinc.

d. *Clear finishes for zinc* (*ZE82*). *De Bell and Richardson Inc.:* Earlier on in this paper, cost centre analysis was mentioned, and this programme is perhaps as good as any to demonstrate its advantages. Zinc in diecast form takes a good polish when treated correctly but tarnishes easily to give a very dull grey finish and, under corrosive conditions, becomes stained with white corrosion products. However, it plates easily, but this is a multistage operation. The question arose, can zinc diecastings be given a high polish mechanically and the surface protected with a weather resistant finish?

The contractors have produced a number of coating systems which give good performance in accelerated corrosion tests and at exposure sites for over two years. Samples are now undergoing environmental testing on lorries in the Detroit, Wilmington, Youngstown and Columbus areas, as well as on tugboats in New York Harbour. Marine testing is under way at Kure Beach and Hazardville. The criterion is five years durability on automotive trim without deterioration. Parallel to this work, methods have been devised to give the highest reflective finishes to zinc diecastings. This has been published as a work manual.

The standard treatment, recommended by the contractor, suggested the following steps for castings made from Zamak 3 (Equivalent UK material, Mazak 3):

Buffing — Water based tripoli

Cleaning —1,1,1,-Trichlorethane vapour, followed by drying for five minutes at 120°C.

Primer

PKHH predried for four hours at 77°C[1]	100 parts by weight
Nitration grade toluene[2] dried with Linde 4A Molecular Sieves	172 parts by weight
Tetrahydro furan DPI 5308[3]	435 parts by weight
Urethane grade cellosolve acetate[4]	540 parts by weight

This 8 per cent solution is applied by flood coating and allowed to dry for 20 hours before stoving for 30 minutes at 120°C.

Top coat

Acryloid B.44 (40% solids)[5]	250 parts by weight
Tinuvin P[6]	5 parts by weight
Silicone R. 12 (50% solids)[7]	0.1 parts by weight
n - Butyl acetate[8]	13.5 parts by weight
Nitration grade toluene	236.5 parts by weight

This solution is diluted to either 8 or 13 per cent non volatiles content with nitration grade toluene. A film thickness of 1.65 to 1.75mil is attained by application of successive coats of the materials; the build up being checked after each coat. After final drying the full coat was stoved for 60 minutes at 80°C followed by 30 minutes at 120°C. This treatment resulted in film shrinkage to the extent of 0.2mil, so giving a final dry film thickness of between 1.45 and 1.55mil.

The contractor suggested a second procedure, which was considered to be an improvement on the above system, taking into consideration the effects due to modifications to the various stages examined in the course of the work, but not examined collectively:

Buffing

1. Cutting as required.
2. Tripoli in bar form on 86/93 loose buffing wheel
3. Alumina colour buff on canton flannel
4. Extra fine colour buff. 2μ Alumina in hard hydrocarbon wax on Domet flannel.

Cleaning

Triple treatment in perchlorethylene vapour bath

Chemical treatment (optional)

Chromate conversion coating

Drying

5 minutes at 120°C.

Primer

Eponol 55-L-32[8]	312
Cellosolve acetate	328
Nitration grade toluene	172
Methyl ethyl ketone	436

Applied at 2mil dry film thickness and stoved for 30 minutes at 120°C.

Intermediate coat

Acryloid B44	250
Permasorb MA[9]	5
Nitration grade toluene	30.5
Benzoyl peroxide	0.1
Heat with stirring 24 hours/80°C under nitrogen add:	
Toluene	620.6
Silicone R.12	0.1
n - Butyl acetate	13.5

Apply 1.15mil by spray on primed metal.

Top coat

Acryloid AT 50[10] (50% solids)	200
Tinuvin P.	5
Solvesso 100	200

Apply at 0.6mil dry film thickness. Stove for 1 hour at 80°C followed by 30 minutes at 135°C to give total dry film thickness of 1.5mil.

These coatings are now available from the Stanley Chemical Co.

e. *The hazing of paints containing zinc oxide* (*ZC95*). *The Paint Research Station:* This programme is now complete and the work published. There is much of interest to the paint chemist in this report, since the information is obviously applicable to other types of surface coating. The importance of moisture in gloss retention is probably one thing that will be of interest, and it was found that the gloss retention of paints containing zinc oxide increases with increasing moisture content up to a maximum of 3 per cent. Another important point was that the volume changes during ageing of a paint containing zinc oxide were only half those of paints pigmented solely with titania.

f. *The painting of sprayed zinc* (*ZM114*). *The Paint Research Station:* This work has been in progress for about 12 months, and has already provided some interesting data on the variability of the sprayed zinc surface. Work is now in hand for a major exposure testing programme to evaluate the effect of zinc surface quality on paint durability and to assess the performance of development paint formulation on standard zinc sprayed surfaces.

g. *Zinc rich paints* (*ZE36*). *Imperial Smelting Corporation:* Five annual reports are available on the work carried out for this contract. Aspects covered are the effect of PVC, type of dust, type of medium and film thickness on durability and weldability. The effect of extenders on the durability of zinc dust primers is also well in hand. Inorganic primers have been examined in some detail, and plans are now in hand to have some of the best formulations obtained tested at Kure Beach and other severe sites in America.

h. *Welding of zinc coated structurals* (*ZM115*). *British Welding Research Association:* With the increasing use of zinc rich and other zinc containing primers in the shipbuilding industry ILZRO has participated in a project to investigate the welding proportion of zinc primed plate.

Ship's plate, primed with a variety of materials, has been welded using both automatic twin fillet, and manual twin fillet and double fillet welding techniques. Radiographic examination of the welds so obtained has been carried out to

assess the amount of porosity present, together with tensile tests on the weld joints. Conclusions reported are that the amount of porosity is conditioned by the method of welding employed and the type of primer. Moreover, it was established that the degree of porosity had no effect on the tensile strength of the joint.

Further work is now in progress on the welding of high duty steels from United States and other sources in a programme sponsored entirely by ILZRO. The programme also includes the welding of galvanised steel by similar means.

i. *Organo-zinc compounds (ZC42). Organic Chemistry Institute TNO, Utrecht:* The evaluation of these materials and the synthesis of certain compounds for specific uses has been proceeding for some years. Much of the synthetic chemistry is of specialised interest only, but certain compounds such as those containing Zn-As and Zn-S bonds are considered as potentially toxic agents against moulds, marine fouling, and algae.

Other compounds have been found to behave as stereospecific polymerisation catalysts and this application appears to have great promise.

j. *Improvements in zinc lithographic plates (ZM4). Lithographic Technical Foundation:* It was decided in the early days of AZI-LIA that the use of zinc sheet for litho plates was one outlet which was at risk, since aluminium had been examined by many printers and found to be satisfactory. At this particular time considerable interest was being shown in a new zinc alloy developed by New Jersey Zinc Co. which contained 0.14 per cent titanium and 0.40 per cent copper, and possessed very good creep resistance and formability. The LTF, in conjunction with three American companies, was asked to co-operate in evaluating this alloy as a litho plate material, and to examine methods of graining and preparation of printed plates.

Flexibility was found to be adequate; a rolling technique was developed and a supply of sheet was evaluated by LTF. The graining of the plate was the first problem to be solved, a tub graining technique being perfected. Practical tests on a machine involving 130,000 impressions followed by 40,000 revolutions under excessive blanket pressure indicated that creep varied between 0 per cent and 0.02 per cent by register rule. Parallel with this work, a new wipe-on plate-making process was developed, and a proving run of 268,000 impressions of 58in x 76in two-colour prints were produced on a Harris press. Concurrently a novel wipe-on process was developed, which has proved extremely successful.

This programme is now complete, patents have been granted and licences issued for commercial development in Europe and the USA.

Lead

The lead programmes in many cases parallel those dealing with zinc.

a. *Lead pigments in water based vehicles, including paints, for surfaces other than non-ferrous. (LC50). Eagle Picher Industries:* This programme has been active for some years now, and has indicated that certain lead pigments in water-based media have real advantages when used as wood primers, particularly on those woods which are prone to staining, such as western red cedar and redwood. With the increasing popularity of wood facings in Europe, the results of this programme merit some attention. Basic lead silicate is showing up well

in this context, and an additional advantage is apparently a very significant decrease in the degree of cracking when compared with solvent based materials.

b. *Antifouling paint formulations (LC81). Battelle Memorial Institute:* This programme is currently examining the antifouling properties of compounds of the type R_3-Pb-X. at sites at Miami Beach, Fla., Pearl Harbour, Hawaii, and Sayville, Long Island, whilst a rather specialised aspect is under examination by ISC at Poole through the good offices of ROSCM.

The results obtained in the USA are very promising, and some formulations containing triphenyl lead and tributyl lead acetates are showing success. The real difficulty in this type of work is that one may have to formulate from scratch, rather than undertake the mere addition or substitution of one ingredient by another. The SS Edinburgh Castle has been test painted with an antifouling paint based on the results of this work.

c. *Lead pigments in electrophoretic paint deposition systems (LC95). Eagle Picher Industries:* This programme is parallel to the zinc activities, but so far few results are to hand.

d. *Organo-lead compounds:* The application of these materials in anti-fouling compositions has already been discussed. But it is of interest to note that compounds of the same type Ph_3-Pb-X are being actively investigated as rot-proofing agents, anthelmintics, polyurethane foam catalysts and as bilharzia control agents.

Dealing with more general programmes, the effect of zinc in nutrition is of vital importance: as a trace element its presence is vital for good health and growth. Zinc deficiency is common in many areas of the world, and a number of exercises are in progress where zinc additions to the diet of animals such as cattle, pigs and fowl are being assessed. In these the object is to ascertain the minimum zinc levels necessary to produce a good animal.

In the medical field the use of zinc as zinc sulphate dosage to accelerate the healing of wounds has been reported on. This increase in granulation rate is enormous, and can cut hospitalisation times by 50 per cent. Bilharzia control in the Middle East is an economic and human necessity; carried through infected water, the Bilharzia worm spends a part of its formulative life using a snail as an intermediate host: kill the snail and the ring of infection is broken. Certain organo-lead compounds will do this at levels which are non-toxic to humans.

Now, what of the future? New fields of research and development on the uses of lead and zinc are being constantly discovered; new attacks are being made on established lead and zinc markets by other materials, but the author is confident that when the major world producers can co-operate to the extent that has been here described, the industries will continue to prosper and to make their contribution to the world's needs in every field.

Acknowledgment

The author gratefully acknowledges the help given him by the Director of Research of ILZRO, Dr S. F. Radtke, and his staff. They have given him every possible encouragement, and permitted him to draw freely on the vast store of information which they have available. Without this help, this address could never have been prepared.

[*Received 2 February 1968*

Lead

Change in use pattern, 1954-64
Consumption in '000 metric tons

	World				Europe				USA			
	1954		1964		1954		1964		1954		1964	
Outlet	Tons	%	Tons	%	Tons	%	Tons	%	Tons	%	Tons	%
Batteries	470	24.6	715	30.4	145	18.1	275	26.0	305	30.8	385	36.1
Cables	375	19.7	390	16.8	235	29.4	270	25.7	115	11.7	50*	4.8
Sheet and pipe	250	13.2	270	11.4	165	21.0	175	16.7	50	4.8	45*	4.1
Pigments and compounds ..	180	9.5	220	9.4	85	10.9	105	9.7	85	8.7	95	8.7
Antiknock compounds	165	8.8	255	10.9	20	2.6	50	4.9	145	14.7	205	19.1
Other uses	460	24.2	495	21.1	140	18.0	180	17.0	290	29.3	290	27.2

Zinc

Change in use pattern, 1954-64
Consumption in '000 metric tons

	World				Europe				USA			
	1954		1964		1954		1964		1954		1964	
	Tons	%	Tons	%	Tons	%	Tons	%	Tons	%	Tons	%
Galvanising	730	37.9	940	33.8	290	31.6	340	26.6	365	40.6	395	34.7
Brass	370	19.2	580	21.0	255	27.7	415	32.5	100	10.9	120	10.6
Diecasting	320	16.7	660	23.8	65	7.1	175	13.8	255	28.2	430	38.0
Rolled zinc	200	10.4	245	8.8	150	16.5	185	14.6	45	4.8	35*	3.3
Zinc oxide	215	11.2	240	8.6	95	10.3	90*	7.3	115	12.8	125	11.1
Other uses	90	4.6	110	4.0	60	6.8	65	7.2	25	2.7	30	2.3

International Lead Zinc Research Organisation Publications

1. *ILZRO Research Digest*

Published annually in five parts:

Part 1. Diecast and Wrought Zinc
Part 2. Zinc for Corrosion Protection
Part 3. Zinc Chemistry
Part 4. Lead Metallurgy
Part 5. Lead Chemistry

These digests contain brief descriptions of work in progress, a list of all completed ILZRO programmes and titles of all published papers dealing with ILZRO work.

2. *Research Reports*

All ILZRO contractors are required to provide quarterly progress reports on their work, together with an annual report. As a general rule these are freely available, but certain areas of work are regarded as confidential and the reports are therefore restricted in circulation. This situation applies only to subjects where patent coverage is likely to be gained.

References

1. Union Carbide Corporation.
2. Sinclair Oil Corporation.
3. Eastman Chemicals.
4. Union Carbide Corporation.
5. Rohm & Haas Inc.
6. Geigy Corporation.
7. Union Carbide Corporation.
8. Shell Chemicals.
9. National Starch Products.
10. Rohm & Haas Inc.

Next month's issue

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

"The composition and some uses of tall oil products," *by K. S. Ennor.*

"An investigation into the relationship between the nature of surface defects and gloss," *by J. H. Colling, W. E. Craker and J. Dunderdale.*

"Antifouling paints based on organotin compounds. Part I," *by L. Chromy and K. Uhacz.*

"The effect of zeta potential on the optical properties of paints," *by M. J. B. Franklin.*

Guest Editorial

This issue contains (p. 479) a Report of the Council Meeting held on 28 February 1968, at which the findings of the Working Party on Forward Thinking were received, one of their recommendations being that such reports should be so published.

As Dr S. H. Bell was President when the project commenced, and was responsible for its instigation, the Editor has invited him to contribute this Guest Editorial.

Where do we go from here?

Will you be around in 2018AD? Some of our present members will be. What changes will they have seen? Many many more than have been seen by the pioneers of our Association who join us in the celebration of our 50th anniversary, extensive though those changes have been.

Sit down, and calmly let the mind wander and wonder. Let it try to predict what the general technical situation (not just in our own technologies) will be five, ten, 25, 50 years ahead. You will find it a stimulating exercise, becoming more baffling the further the mind is projected into the future, but if any startling ideas emerge that disturb the calm, make a note of them for it will be interesting to check up later. After a mental projection of more than ten years or so the mind begins to boggle, especially if the assumption is made that the rate of change will increasingly increase and if the exercise is preceded by contemplation of developments during the last not very many years—computers, automation, heart-transplants, space travel, colour television, seeing the back of the moon, atomic power, jumbo jets, the information explosion, miniaturisation, communication satellites, and so on and so on, to say nothing of ordinary chemistry and physics and our own technologies.

It was this kind of mental browsing on the past and future, stimulated by many conversations with friends, that led me, when I became President in 1965, to wonder about OCCA and to try to assess where we stood at that time, how we got there and whence we should be travelling. It was clear that we ought to be responsive to the merits of possible changes and developments, and able to judge possibilities soundly in a world rapidly changing scientifically, technically, industrially and financially.

It was particularly valuable to be able to do this whilst standing on firm ground—on the strength of OCCA as established over the years, rather than from weakness and any need for sudden changes. Were there nevertheless some gaps in our activities, left by the concentration of our energies in various established directions? There was no thought of doing other than continuing to build on our successes—the *Journal*, the Exhibitions, the Conferences, the great work of the Sections and Branches; possibly to review them with the future in mind, but mainly to consider what else we ought to be doing and the inter-relation of all our activities. Though much was being done by Sections, and centrally through the publication of the Training Manuals and the Introduction to Paint Technology, were we making an adequate contribution to education and training? These and many other questions came to mind.

Many OCCA members have thought deeply about the future, and taken action, as the history of our Association shows, but a survey right across the board seemed likely to be of value, and the Officers were enlisted to give their ideas over the whole field, not just over those parts of it for which they were individually responsible. The result was a document called "Forward Thinking"—a title borrowed appropriately from a much earlier document prepared by Dr L. A. Jordan as Director of the Paint Research Association, covering some post-war thoughts on the technical future of the industry. It derived from his own habit of mind which he always tried to engender in his staff. The choice was also frankly tactical—so much better than such a title as "Memorandum on Present Activities and Future Possibilities"—as likely to be applied

not just to the document but to the whole exercise which it was hoped would lead to wide participation in many forms, and then to action.

The response of the Council was most gratifying and almost immediately Sections held meetings and sent in reports on all the subjects and ideas covered. Subsequently working parties were formed and already some of their recommendations have been adopted as can be seen by the reports elsewhere in this issue of the *Journal*, though other recommendations will take longer to consider and some have not yet been framed. The rapid response is in itself a tribute to the vitality of OCCA and the enthusiasm of those members participating, for the original "Forward Thinking" report went to Council on 20 April 1967. Section reports on it were available by 28 November 1967, the first working party report went to Council 28 February 1968, and action has already been taken.

The Hon. Editor kindly invited me to write these few words about what seem to me to be matters of great significance, the need for our having a forward-looking attitude in these days, and the evidence of the enthusiasm displayed by all concerned to do things for our Association. It gives me also an opportunity publicly to thank them on behalf of all our members. So many have contributed that I have hesitated to mention names for fear of omission, but special tribute is due to the Hon. Secretary, Mr Bews, who prepared a working draft of the first memorandum on behalf of the Officers, Mr Moll who so ably leads the main working party, and Mr Hamblin, our Director & Secretary, for his assistance at all stages.

We bear on our insignia the head of Leonardo da Vinci, poet, artist, architect, scientist, who predicted or anticipated numerous developments in engineering, aviation and much else; a forward-looking genius. Our insignia also bears the words "Et Mente Et Manu"—with mind and hand—thinking and action.

S.H.B.

Review

Organic Chemistry of Macromolecules

An Introductory Textbook by A. Ravve. London: Edward Arnold (Publishers) Ltd., 1967. Pp. xiii+498. Price £7 10s.

This book is laid out on classical lines. An introductory section on history, definitions, physical properties and molecular weights is followed by sections on addition polymerisation mechanism, common addition polymers, condensation polymers, naturally occurring polymers, and reactions of polymers. Each of these is broken down logically and discussed in some detail. Particularly interesting chapters are those on ladder polymers and polynucleotides. Apart from a general sparsity of references to industry, and particularly to the industrial importance of individual polymers, most of what one expects to find is there. Unfortunately, much that one does not expect to find is also there.

At first view, the work seems thorough, erudite, and even sophisticated; but appearances are deceptive, for it abounds in mistaken and misleading statements, half-truths and inconsistencies, not all of which are attributable to the multitude of misprints which stalk its pages. A catalogue of these would occupy more space than we have available, but some typical examples follow. There is a very real danger that the beginner (and remember, this is an *introductory* textbook) will be conditioned to think along unsound lines from the outset. This is a disappointment and a crying shame, for an immense amount of work has gone into collating the stuff of which really good textbooks are made, and has been reduced to nought through carelessness.

Some of the errors merely demonstrate slipshod workmanship and do little harm, since they will be detected by any tyro. Polacetal, sebasic, oxydation, tartarate, pentaerythrilol, viscinally, kitenimine, cycolise, KcN, treosyndiotactic, glulathione, polyethylidine and stochiometric are a few of these. On a first reading, we found 24 such errors between pages 244 and 283, an average of one per 1.8 pages. Disrespectful, if still not too harmful, is the mis-spelling of names like Bechmann and Beckman (for Beckmann), Bambord (for Bamford), Megason (for Megson) and Losson (for Lossen). Incidentally, Smekal's *Lockerstellen* theory is attributed to Houwink.

Rather more concern is caused by errors which *could* be attributable to the compositor but seem more likely to have originated in the manuscript, and which are less obvious to the beginner. Repeated references to pyrrolidine (instead of pyrrolidone) as a lactam and to sulphonic acid (in context a definite compound) as a catalyst are typical. One is no less worried by two illustrations of crystalline "polyacrylonite" and "polyethelene," attributed to Peterlin, but not to be found in the reference given. Whether misprints or something worse, incorrect algebraic formulae which mysteriously lead to the correct conclusion (p. 246), and correct algebra which somehow yields an incorrect answer (p. 248) do little to engender faith in the book. Then, what faith one has, suffers a severe blow on p. 278, where the depicted route to nylon 12 contains four glaring errors (lauryl lactam and the nylon 12 repeat unit each apparently contain only five carbon atoms, peracetic acid is formulated as acetaldehyde, and the route passes through an impossible intermediate).

All this is bad enough, but still more serious damage is done by carelessly worded phrases and sloppy illustrations which offend the laws of chemistry and logic, to say nothing of language and common sense. Thus, on p. 22, chain folding in crystalline polymers occurs "because the chain direction is 100A in the thin lamellae and the chain length is 20,000 to 30,000A"; on p. 25, "Styrene, for example, can be synthesised in two forms, isotactic and atactic"; on p. 13, a "network polymer" is shown as having an open chain structure with some suggestion of branching but none of cross-linking, and, on p. 35, vulcanised rubber is depicted as a ladder polymer. Having been weaned on these gems, the student is then invited to absorb such inconsistencies as the statements, on p. 261, that "five membered lactones fail to polymerise" but that "butyrolactone will polymerise quite rapidly"; or, on p. 264, that "——now achieving industrial significance is an aromatic sulphone," illustrated by the structural formula of a polysulphonate. As examples of phrases which, literally, are sheer nonsense, one may mention, "reactivity decreases with increase in the size of the aldehyde" (p. 324), "halogen replacement of α-carbon" (p. 390), and "tertiary hydrogen atoms which are weaker than average carbon to carbon bonds" (p. 469). A final pearl of the English (or American) language may be quoted from the discussion of pvc degradation: "Once radical attack occurred and unsaturation was produced, then the adjacent methylene groups to the liberated chlorine atoms become allylic and, therefore, possessing labile hydrogen atoms."

We suspect that the book free from misprints has yet to be produced, and would admit that the occasional howler can pass behind a pitying smile. But this is ridiculous.

A. R. H. TAWN

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.)*

BASF (UK) Ltd. have recently announced that they have renamed their *Colonyl* range of pigment dispersions. These are now to be known as *Luconyl* colours. At the same time the range has been supplemented by the following products: *Luconyl Yellow G, Luconyl Orange RN, Luconyl Red FGR, Luconyl Red BB, Luconyl Blue LBGO, Luconyl Black N.* The range of *Pigmosol* colours, in powder or flake form, has been supplemented by the addition of *Pigmosol Yellow 10G, Pigmosol Yellow 10G Flakes, Pigmosol Yellow G, Pigmosol Orange RN, Pigmosol Scarlet RNC, Pigmosol Red FGR.* Both ranges have been developed for water based formulations.

A new range of clear and opaque colour coatings for glass has recently been announced by **Swale Chemicals Ltd.**

The new *Spectracote* coatings can economically be coated on to clear glass stock, enabling limited runs of coloured glass containers a practical and economical proposition. The coatings are claimed to have outstanding product resistance, excellent adhesion and scratch-resistance, and good colour retention.

A new method of heating reaction vessels has been developed by **Hygrotherm Engineering Ltd.** The method, which is claimed to be one of the cheapest and safest methods of heating vessels in the range 100-400°C, is based on the use of combustion gases from the *Hygrotherm R-Burner*, which is suitable for use with fuel oil, natural or town gas. The combustion gases are circulated at high velocity through half coils welded to the outside of the vessel, or coil or plate heat exchangers immersed in the material to be heated. The velocity of the combustion gases is so high, it is claimed, that very high film coefficients are attainable.

Bakelite Xylonite Limited, Plastics Materials Group, has recently introduced two new series of colour masterbatches for polyethylene film, which, it is claimed, give low cost, bold bright colours having good print contrast in polyethylene films.

The *PZ 131* series is designed for good dispersion in film over 500 gauge, for heavy duty applications, while the *PZ 147* series is designed to give opaque or near opaque film between 200-400 gauge.

A new barium free red toner, *Irgalite Red 2BY (AT)*, is announced by **Geigy (UK) Limited.** It is a yellow shade red toner, supplied in powder form, and, as it meets both the Home Office Statutory Instrument No 1157/1967 and BS 3443:1961 (safety requirements for children's toys and playthings) it is specially suited for toy finishes.

Spelthorne Metals Ltd. has recently published a report, illustrated in colour, of a five-year exposure test on seven different formulations of metallic lead primer. A high order of protection is claimed for both gritblasted and weathered steel substrates.

Copies of the report (ref SL 229), which is printed in English, French and German, are available from Spelthorne.

The Pyrene Company Limited has recently published a leaflet describing the *Bonderizing* process for metal. Processes for steel, aluminium, zinc and mixed metals are detailed.

Also from Pyrene is *Sales Information Bulletin No 37*, on *Preperite*, a thixotropic preparation developed for "spot" de-rusting where it is unnecessary or inconvenient to immerse the complete component in a de-rusting solution.

Play safe

Irgalite® AT pigments
Analytically tested to ensure safety in use

Introducing Irgalite Red 2BY AT
a bright yellow shade red 2B toner free from barium particularly suitable for full strength toy finishes

Recommended for
school materials
pencils and crayons
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The Irgalite AT range also includes
Irgalite Red 2G AT
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Irgalite Yellow GS AT
Irgalite Yellow 5GG AT
Irgalite Yellow BAW AT
Irgalite Orange P AT
Irgalite Maroon BN AT
Irgalite Scarlet RNP AT

Geigy

Geigy (U.K.) Limited
Pigments Division
Simonsway
Manchester 22

Roskydal UV 10 is the first photo-polymerizable unsaturated polyester resin on the market, claim **Farbenfabriken Bayer AG.** Curing requires neither cobalt accelerator nor organic peroxide, and can be effected by exposure to light sources such as super-actinic flourescent lamps and high-pressure mercury vapour reflector lamps. Curing times of 30 seconds are said to be possible. One-can finishes based on *Roskydal UV 10* can, it is claimed, be applied in the usual viscosities by all curtain coating and spraying processes customary for unsaturated polyester resin finishes.

Davidson & Co. Ltd., of Belfast, are now manufacturing and marketing the *Davidson-Gayco Classifier*, under licence from the **Universal Road Machinery Co.** of New York. The unit is designed for high-efficiency separation of any dry granular or powdered material, and is said to enable the fineness of products from grinding mills to be continuously controlled within very close limits.

A new range of industrial drying cabinets has recently been announced by **Pratchitt Brothers Limited,** a member of the LAM Group, and the first model is now available. New design features include accurate temperature control using a potentiometric controller with an integral process timer, an integral cubicle, outside the heated chamber, housing all controls, instruments and motors, etc, and high efficiency insulation, including silicone rubber door seals, to minimise heat loss. Maximum temperature is 100°C, and steam or electric heating may be used.

Bowmans Chemicals Limited have recently revised their data sheet entitled *Lactic Acid and Lactates in Food and Drink*. Copies are available from Bowmans on request.

It has been announced that, as at 27 March 1968, **The Wilson-Bennett Company Limited** will take over the whole of business, property, rights, undertaking and assets of **Donald Macpherson & Co. Ltd.,** of which it is a subsidiary.

Wilson-Bennett will then take the name of **Donald Macpherson & Co. Ltd.,** and the parent company will become **Donald Macpherson Group Limited.** The freehold and leasehold properties of the old Donald Macpherson & Co. Ltd. will be occupied by the new Donald Macpherson & Co. Ltd., although these have not been transferred, and the relationship between the two new companies will be the same as that between the two original companies.

Evans Electroselenium Limited have recently announced the publication of a quarterly publication, "EEL Bulletin," giving latest information on EEL instruments, and news pertinent to their use.

Readers can be placed on the circulation list on application to the editor of the bulletin.

Hercules Powder Company Limited have recently announced that they have acquired the share capital of **Fredk. Boehm Limited** and its subsidiaries. Fredk. Boehm Limited will continue to operate as a separate company under its present management, and the Fredk. Boehm Board will join the Board of Hercules Powder Company.

A new company, **Paklite Ltd.,** has recently been formed to manufacture pvc bottles and containers, and plastisols. Paklite is connected with **Britiona Limited,** of North London, and is situated in Bletchley, Bucks.

A combined report of the work of **The British Paper & Board Industry Research Association** (BPBIRA) and **The Printing, Packaging & Allied Trades Research Associa-**

tion (PATRA) during the year leading up their fusion on 29 June 1967 as **The Research Association for the Paper & Board, Printing & Packaging Industries** (PIRA), has recently been issued by PIRA.

The *Thermonitor*, the instrument for temperature control which, when used in conjunction with a mercury-glass thermometer and an electrical heater or cooler, is claimed to be capable of controlling temperature to an accuracy of 2mm linear thermometer scale, has been improved for 1968, claims the maker, **GSPK (Electronics) Ltd.** The instrument is now smaller and more compact, and the console has been improved for easier adjustments.

Elga Products Limited recently presented a new addition to their range of water purifiers, the *Elgacan*.

The *Elgacan* features a dispersable deioniser complete with a disperser for wall mounting and quality control, with tube for direct connection to existing water supplies.

Pure water is available at the turn of a tap. Effluent quality is monitored on a small battery operated meter. Output per can varies according to the quality of the raw water, and figures of 328 litres for Manchester and 72 litres for Cardiff are quoted. The low cost of the equipment, and the fact that no regeneration on site or cartridge service is required, are said to make the *Elgacan* a breakthrough in the field of water purification.

Hull

Paint, art, colour and heraldry

The fifth ordinary meeting of the session took place at the Queens Hotel, Hull, on 5 February when the Chairman, Mr L. W. Wynn, introduced Dr S. H. Bell, the Immediate Past President, who gave a lecture on "Paint, art, colour and heraldry."

The lecture was extremely well illustrated with some 80 colour slides, all taken by Dr Bell, and was, therefore, to a large extent visual. In the first part of the lecture, Dr Bell considered the technical requirements of paint for pictures as illustrated by the Old Masters and pointed out the very different rheological requirements as compared to decorating. The artist obtained many of his effects by his brush technique, so that brush marks must persist, and flow out after application was not required. An infinite colour range was necessary, but these the artist mixed himself from a limited number of colours. A high opacity was not always necessary and many effects were obtained by the lack of hiding power.

Dr Bell then turned to the way in which a metal object in a painting was made to look metallic and distinguishable from, for instance, porcelain. This was controlled almost entirely by the intensity and colour of the highlights and corresponded closely to the known optical behaviour of the materials concerned. The effect was illustrated by a series of colour slides of panels and miscellaneous objects photographed for this purpose.

In the second part of the lecture, the origin and development of heraldry was described, and the formalised descriptive method discussed. A number of Coats of Arms used by various organisations and companies were illustrated and in many cases their meaning explained.

A vote of thanks was proposed by Mr E. Armstrong for a most interesting, enjoyable and excellently presented lecture. This was warmly supported by the 19 members and 18 visitors present. The lecture was followed by light refreshments, during which many of the audience discussed the subject with Dr Bell.

S.R.F.

Towards automation

Mr H. R. Touchin gave a paper entitled "Towards automation" to the sixth ordinary meeting of the session, held at the College of Technology, Hull on 4 March. The section Chairman, Mr L. W. Wynn, introduced the speaker.

Mr Touchin first stressed the difference between mechanisation and automation. A drilling machine could easily be arranged to go on drilling holes at the correct points on a sheet of metal, this was mechanisation and continued irrespective of whether or not the holes were coming out the right size. The essential difference was that in an automated system some form of sensing device was incorporated to compare the hole made with some standard, and a "feed back" used to stop the drill when the hole size was no longer correct.

Turning to our industry, it would be a near impossibility to take a paint factory and automate all its operations; the logical approach was to seek those areas where automation could be adopted with the greatest advantage, e.g., where labour costs were high, and for repetitive operations, to adopt it in these places and to extend in the light of experience gained to other fruitful places.

The types of equipment available to perform various operations were discussed and illustrated by diagrams. Plenty of equipment had been developed with which the

input variables, time, temperature, speed, power etc. could be controlled, but the control of quality might become more difficult; colour, density and viscosity could probably be controlled, although paint presented some special difficulties on account of its opacity and stickiness, which could make sensing devices inoperative. The control of brushability and dry film properties etc. presented problems which had not yet been solved.

The meeting was followed by a discussion in which Messrs Robinson, Gilroy, Brown, Pulford, Read, Wenham and Armstrong took part.

A vote of thanks was proposed by Mr E. Armstrong and was well supported by the 16 members and one visitor present.

S.R.F.

London

Co-operation—a necessity for paint and printing ink research

A technical meeting was held on Thursday 21 March 1968 at University College, London WC1, with Mr R. N. Wheeler in the chair. Mr H. K. Raaschou Nielsen, Director of the Danish Central Paint Research Laboratories, gave the Annual European Liaison Lecture on "Co-operation—a necessity for paint and printing ink research."

Mr Raaschou Nielsen described the Danish Paint and Ink Research Laboratory and its functions in relation to the industries it served. There was complete co-operation between the Danish and the Swedish central research laboratories, both in the co-ordination of their research programmes and in the fact that any problem arising from the industry could be sent to whichever of the laboratories was best equipped for the purpose.

Mr Raaschou Nielsen continued by describing the setting up of the various European committees, e.g., the European Committee for Paint and Printing Ink Manufacturers Associations (1952), and the ISO Technical Committee (1963). Close co-operation occurred amongst the seven national paint research laboratories in Europe, and joint investigations on glass transition temperatures and on durability of paint systems in different climates are being carried out.

There were also close relations with universities and technical colleges, including the provision of special courses for students wishing to specialise in paint or printing ink technology. This co-operation was a two-way affair, and the institute had facilities for advanced research provided by the Institute of Chemical Industries at the University of Copenhagen.

Examples were given of other types of co-operative work, with raw material manufacturers, consumers and technical societies. In the discussion following the paper, those taking part included Dr L. Valentine, Dr W. Carr, Dr S. H. Bell, Dr G. L. Fuchs, Mr N. Fisk, Mr T. R. Bullett, Mr J. K. B. Butler, Mr J. L. Hawkey, Mr J. E. Pooley and Dr R. H. Leach. A vote of thanks was proposed by Dr S. H. Bell.

V.T.C.

Manchester

Instrumental colour matching

At a meeting on 8 March 1968, at the Liverpool Building and Design Centre, three speakers, Mr R. Smith (Goodlass-Wall), Mr A. J. Ford (Blundell-Permoglaze) and Mr I. Ford (Donald MacPherson), each took one aspect of the above subject. Mr I. S. Moll was in the Chair, and 53 members and guests were present.

Mr R. Smith, the first speaker, gave a general introduction to the subjects of colour and colour measurement. He pointed out that the specification of a colour

required information on the reflectivity of the coloured surface, the energy distribution of the illuminant, and the response of the observer. The first two parts could be measured objectively, using, for example, 32 parameters; the last, involving three visual receptors in the eye, could be expressed only by three parameters. Spectrophotometry provided objective measurements. Colorimetry which provided three parameters was comparable to subjective observation. Both types of instrument could be used to provide colour difference measurements, leading to the use of such units as Modified Adams and MacAdam.

Mr Smith then turned to the use of spectrophotometers in the colour correction of paint batches. The method he described used the Kubelka-Munk formula to derive the basic expression—

$$\frac{(1 - \Delta R)^2}{2\Delta R} = \Delta\theta = \Delta C_a K_a + \Delta C_b K_b + \Delta C_c K_c$$

which, containing three unknowns (ΔC_a, ΔC_b, ΔC_c) required use at three separate wavelengths to obtain solutions. The achievements of the system were—more uniform colour control, permanent records, avoidance of colour drift of standards, speed up in production, and prevention of the use of unauthorised pigments for shade corrections. The chief limitation was to the lighter colours because of the simplified theory used, and because of instrument sensitivity. Improvements foreseen were in the field of instruments where lower cost, higher sensitivity and stability were achievable.

Mr A. J. Ford then described the use of the COMIC analogue computer for recipe prediction and batch control. In both fields, lower paint manufacturing costs could be achieved, in the first place by assuring that the most economic formulation was used. The operation of the computer was described, non-metameric matches being straightforward matching of the reflectance curve on the display tube, metameric matches requiring the additional use of the tristimulus digital computer. In recipe prediction, a cost index could be introduced by sacrificing one of the 16 wavelengths normally used. Mr Ford's experience was that in batch correction 70 per cent of matches to standards took one correction step, and that no more than two steps were necessary.

Mr I. Ford discussed the use of colour measuring instruments to decide acceptability of matches. Using a tristimulus colorimeter (Colormaster) to obtain ΔG, ΔR, ΔB for a sample against a standard, these were transformed into ΔL, Δa, Δb for the modified Adams expression, by using an analogue computer, and finally converted to a colour difference, ΔE, by using a desk calculator. This he described as a control system. A complete system involved the use of a digital computer at much higher capital cost. This system enabled acceptable matches to be defined, reduced batch-to-batch variation, and through recorded results, defined the systems accuracy, and also indicated if improvement was required.

There then followed a full hour of general discussion in which all three speakers, sometimes in sequence, answered questions from the enthusiastic audience. At the close, the vote of thanks was proposed by Mr C. Barker and carried with acclamation.

D.A.P.

Midlands

Newton Friend Lecture: Furs

Each session the Midlands Section holds a meeting to which ladies are invited and the subject of the lecture is chosen as likely to be of interest to the ladies. The 12th Newton Friend Lecture was held on 15 March, at Birmingham Chamber of Commerce, when a talk on furs was given by Mr G. N. Smith.

Mr Smith said that furs could be classified according to length of hair or according to wearing properties. Long-haired furs like fox, lynx, skunk and snow-leopard were no longer in fashion and were now only used in collars. Medium-haired furs included sable, mink, marmot, ermine, martins, musquash and Russian squirrel. Examples of flat-haired furs were pony, Brazilian otter, Canadian squirrel and seal. Animals which spent part of their life in water gave long-wearing furs which were water repellent, whilst furs from animals which lived in trees were not long-wearing. For everyday wear, long-wearing furs like musquash, beaver lamb, Persian lamb, nutria, seal, ocelot, leopard and pony skin were suitable whilst the beautiful light-wearing furs like chinchilla and broadtail were best reserved for special occasions.

Furs could be either natural or ranched. When wild animals were trapped, dead-fall traps were used to avoid damage to the skin. Ranching gave control over colour and quality and permitted pelting at the right time. By exploiting mutations, new colours could be evolved.

The furs were then sold at central auctions or were dressed and sold in graded bundles by skin merchants. The furrier, who had served a 12-year apprenticeship, usually began the making of a coat by "stranding" the fur. In this process he cut the fur into thin strips, sloping from the spine. The strips were then sewn together, but displaced about ¼in from the original position. This increased the overall length by 50 per cent and emphasised the pattern along the spine. The stranding of furs for a coat could take up to three weeks and the sewing together a further three weeks. A mink coat required six miles of cotton and up to 80 pelts. The assembled furs were then put on a board, dampened and nailed to a pattern. After leaving to dry naturally, the coat was taken from the board, "cleaned off" and lined with Japanese silk or nylon. Not all furs were stranded, some being worked solid, dyed and the pattern put on afterwards.

Most furs came from animals native to America or Russia, except for the spotted animals like the Indian cheetah, the African leopard and the South American ocelot. Spotted animals were becoming rarer as more and more of the land where they bred was taken for cultivation. An international seal-pact, which restricted the number of seals to be taken for furs each year, had saved the Alaskan seal from extinction. Moleskin was the only recognised fur from a British wild animal. Broadtail furs came from Persian lambs which were newly born. Mink was a deep rich mid-brown in the natural state, but by selective in-breeding a range of 40 recognised shades, from white to dark brown, had been evolved.

With his wife acting as a model, Mr Smith then showed a range of very beautiful and very expensive fur coats, including several minks, ermine, Canadian squirrel, Persian lamb, ponyskin and ocelot.

The speaker concluded with some advice on the care of fur coats. The coat should be sent to be cleaned every year at the end of the season. The furrier should be asked to effect minor repairs and modifications according to fashion. Worn skins could be replaced but the obtaining of furs of the right colour and age could take some time.

After the speaker had dealt with a number of queries from members and their ladies, Mr H. J. Griffiths proposed a vote of thanks to Mr Smith for a most interesting talk.

Scottish

Instrumental measurement of colour

The last technical meeting of the Scottish Section for the 1967-68 session was held in the Lorne Hotel, Glasgow, on 14 March, when Mr J. Beresford of Geigy (UK) Ltd. gave a lecture on "Instrumental measurement of colour."

Introducing his talk, Mr Beresford stressed the over-riding importance of the eye, as no matter what an instrument showed, if the results differed from visual observation, the instrument must be wrong. He described the development of standards for illuminants and light sources by the CIE (Commission Internationale de l'Eclairage) and compared data for the 2deg and 10deg fields of vision. He also briefly considered the mechanism of the eye, drawing attention to an important factor in the distribution of the light-sensitive cells across the retina as a consequence of which detailed colour vision was observed only in the centre of the field of view.

Referring to the red, green and blue primaries, Mr Beresford dealt next with the validity of the principle of additive colour mixing in colorimetry and explained the units and some equations employed.

Turning to spectrophotometry, he illustrated the difference between additive and subtractive colour mixing by considering the spectral curves concerned. Those for real dyes showed that the greater the dye concentration, the lower the reflectance curves in particular regions. The relations of reflectance and illuminations was described, and the Kubelka-Munk equation discussed.

Illustrating the differences between this method of colour assessment and visual assessment, Mr Beresford said that observers had been asked to give numerical assessments of strength and it was found that the spectrophotometric results and visual results agreed quite well, for pure strength differences, up to 5 per cent depths. He also discussed the non-linearity of the curve of K/S against concentration; he thought that the non-linearity was important although in application all the colour match prediction methods had a way of getting round it.

At some stage it was necessary to measure the pattern, and with all instruments there was a limit to the smallness of the pattern that could be measured. In an investigation of the measurement of small patterns, it was felt that it was the relationship between the depth of the background colour and that of the pattern that was the problem. By choosing the background depth carefully, it was found that small patterns could be measured reasonably, and also combinations such as gloss/gloss, gloss/matt and matt/gloss were studied. It was concluded that the method should work if three conditions were satisfied: the surface state of the background should be similar to that of the pattern, the brightness of the background must be similar to that of the pattern, and the pattern must be small enough to be covered by the spectrophotometer beam.

Discussing surface reflectance effects, Mr Beresford referred to differences in reflectance of patterns observed before and after weathering tests of phthalocyanine blue. As it could not be believed that phthalocyanine blue had faded, it was found that the reason for the differences was that the paint film concerned started with a high finish and came out of the test looking as though it had been "sand blasted."

Finally, the lecturer discussed problems arising in match prediction with fluorescent colours. These created their effects by a combination of additive and subtractive colour mixing, and therefore the existing mathematics did not apply.

In the discussion which followed, Mr Beresford was questioned closely about the details of his work on the comparison of instrumental and visual colour assessment. He also speculated on the future applications of instrumental colour measurement, and discussed the topics of tolerances and instrumental errors, pointing out that recipe prediction was a less demanding application than measurement of colour standards, and that pale shades were more amenable than deep ones. The meeting closed with a vote of thanks from Mr T. Hannah.

J.D.E.

Eastern Branch

The analysis and composition of triglycerides

The fifth ordinary meeting of the session took the form of a joint meeting with the Society of Chemical Industry, Oil and Fats Group. The meeting was held in the North British Hotel, Edinburgh, with Mr G. H. Hutchinson in the chair, on Wednesday 28 February 1968, when Dr F. D. Gunstone of St. Andrews University lectured on "The analysis and composition of triglycerides."

Dr Gunstone commenced by saying that the last decade had seen renewed interest and activity in the study of glyceride composition. New methods of study had been devised and the interesting results obtained had provided a new insight into the ways in which acyl groups were arranged in natural glyceride mixtures. Dr Gunstone then went on to review briefly these methods and results.

The classical oxidation procedure of Hilditch and Lea had been further improved and developed. In this method fats were oxidised by the von Rudloff procedure. Unsaturated glycerides were thereby converted to azelao-glycerides which were then esterified. The resulting mixture could be examined in a variety of ways, but most informatively by gas-liquid chromatography. Since the major unsaturated acids were oxidised to azelaic acid and could no longer be distinguished this technique was most valuable for fats (such as cocoa butter) having appreciable proportions of saturated acids and only a small amount of unsaturated acids, preferably only oleic acid.

Some progress had been made towards the ideal solution of separating fats completely and quantitatively into their individual glycerides. Three chromatographic methods showed promise.

Glycerides having one, two, three, four or more double bonds could be separated from one another by silver ion chromatography. It was even possible to separate different glycerides with the same number of double bonds. For example, among glycerides with four double bonds those with two linoleic and one saturated acyl group had lower Rf value than those with one linoleic and two oleic acyl groups. Separation was not complete but concentrates beyond 80 per cent were readily obtained and this method had been extensively employed in several research laboratories.

Glycerides differing in partition coefficient could be separated by liquid partition chromatography. This method was likely to be useful but had not yet been widely used.

Glycerides had also been separated by gas liquid chromatography and with careful attention to experimental detail this method could furnish valuable results. Silicone elastomers were used as the stationary phase at temperatures up to about 325°C. Under these conditions separation depended on the chain lengths of the acyl group and difference in unsaturation could not be detected. It was, however, possible to separate glycerides with up to 68 carbon atoms which differed by only a single carbon atom. This method was most informative for fats with component acids having a wide range of chain length such as milk fats (C_4-C_{18}), certain nut oils (C_8-C_{18}), and fish oils (C_{14}-C_{24}). It was less useful for those seed fats and vegetable oils containing only C_{16} and C_{18} acids.

A completely different approach to this problem involved the selective and specific deacylation of glycerides by enzymes. Pancreatic lipase, for example, catalysed the hydrolysis of acyl groups attached to the two primary glycerol hydroxyl groups. The resulting 2-monoglyceride was readily isolated and its acyl groups identified. This provides information about the acyl groups attached at C(2) of glycerol and, by difference, at C(1) and C(3). Methods of computing glyceride composition from lipolysis results had been reported, but the main value of this approach was that it showed, for the first time, that in *vegetable fats*, unsaturated C_{18} acids, and especially linoleic acid, occurred preferentially at C(2). These acids generally made up more

than 95 per cent of the acids at the 2-position. Saturated acids and unsaturated C_{20} and C_{22} acids were almost entirely confined to the C(1) and C(3) hydroxyls unless the content of unsaturated C_{18} acids was below 33 per cent. The lipolysis reaction was simple to carry out and has been widely used.

Brockerhoff extended this enzymatic procedure and reported methods for determining separately the acyl groups attached to each of the three hydroxyl groups of glycerol. These methods were still in the development stage.

The results obtained by these procedures indicated new patterns of acyl group distribution. No clear picture had yet emerged for animal fats but most vegetable fats seemed to conform to the 2-random 1, 3-random distribution pattern. According to this the acids present at C(2) were combined statistically with those at C(1) and C(3). The composition of the acids at these positions could be determined by lipolysis or could be calculated directly from the acid composition of the whole fat on the basis of certain generalisations which had been made. This distribution pattern brought together the previously discordant views of random and widest (even) distribution.

A lively discussion followed. The vote of thanks for an interesting and instructive lecture was proposed by Dr Hudson, the Chairman of the Oil and Fats Group of the SCI.

J.H.S.

Thames Valley

30 Years in polymers

The January meeting, held on 23 January was well attended and took place at the usual venue, The Royal White Hart in Beaconsfield.

The speaker, Professor J. J. Reynolds, began by saying that apart from developing new products, much research into polymers had been associated with improvements to properties and a lowering in cost, irrespective of whether the end use lay in plastics, textiles or surface coatings. As an example he cited the case of polyethylene, which had continually fallen in price over the years with the introduction of improved grades, so much so that many traditional metalware articles had been largely supplanted by polyethylene alternatives. A further demonstration of the continual replacement of the natural product was the fact that 21 per cent of all fibre usage in the UK was now of synthetic origin.

Professor Reynolds then went on to describe some of his earlier chemical associations; the search for new chemical derivatives of rubber, with the low price of the natural product as the incentive; the development of a process for the permanent waterproofing of cellulose textiles, which required processing conditions comparable with those of the Tootal crease-proofing process; the early development of methacrylic esters and the observation by Rowland Hill that the methyl ester formed a clear glossy plastic; emulsions of the polyesters could be used for textile finishes.

Among his interesting experiences during the war years was the discovery of one of the first polyurethane elastomers, namely Vulcaprene A, which was both oil resistant and impermeable to hydrogen. It was amusing to recall that in this development period much time was spent ridding the elastomer of bubbles, when the mixture was in fact an unrecognised polyurethane foam. During the war period too, Professor Reynolds was also involved in the beginnings of polyesters as fibre forming materials and particularly in the early development of commercial routes to Terylene polymer and means of characterising and controlling the quality of the end product. Yet another project involved derivatives of pentaerythritol leading up to interesting polymers, one of which, a polyether, the Hercules Powder Co. later discovered independently and developed as "Penton."

More recently he had been concerned in the setting up of the Petrochemical and Polymer Laboratory of ICI Limited in Runcorn and with some of the long range research projects taking place there. He selected two or three as interesting examples of this period.

First was a development from heat resistant polyimides. The DuPont Co. of America developed an imide polymer, based on pyromellitic dianhydride and diaminodiphenyl ether ("Kapton"). At an intermediate stage the condensate was generally soluble only in highly polar solvents such as dimethyl formamide, but Professor Reynolds and his team recognised the possibility of forming solutions in aqueous amines by virtue of the presence of the carboxyl groups in the precondensate; such solutions could be used for polyimide fabrication.

Another programme involved the study of some cationic polyelectrolytes (potentially useful as surfactants and thickeners), based on water-soluble cationic polymers such as the quaternary salt of pyridine and polyvinyl chloroacetate. These could be cross-linked by the use of ditertiary amines along with the pyridine.

A third topic investigated was a new system of polymer grafting based on some earlier original work by Bamford. Vinyl polymerisation was initiated by metal carbonyls in conjunction with reactive organic halides in which there were several Cl atoms attached to one carbon, or the halogen was attached to an electron with drawing group. By halogenation of the—CONH— groups (on the N atom) and use of metal carbonyls a number of vinyl and acrylic monomers had been grafted onto silk, wool, nylon, etc.

Professor Reynolds ended with a few brief references to his new post at Loughborough University, as head of an Institute of Polymer Technology. It was expected that eventually there would be about 60 post graduate students, either studying for MSc or carrying out research on problems of the rubber and plastic industries.

Questions were put by Messrs Henderson, Walker, Hemsley, Pearson and Gunn, and during this period Professor Reynolds mentioned some of the main aims of his new department. These are worth stating.

(1) To train polymer technologists from graduates in physical, chemical and engineering disciplines.

(2) To carry out research on programmes that might be applicable to the polymer manufacturing and user industries.

(3) Characterisation of the physical, chemical and engineering properties of importance in ultimate performance.

Specific items mentioned as possible research topics were

(a) The greater understanding and the extended application of dispersions.

(b) Polymerisation *in situ* in the fabrication process.

(c) Improved control in polymer grafting.

(d) An improved appreciation of blending reactions.

(e) Studies of fire-resistance with particular reference to polymer structure.

The meeting finally concluded with a warm vote of thanks by Dr G. M. Henderson, one of his former colleagues.

R.E.G.

OCCA 20

The official party at the entrance to the exhibition (left to right): The President, Mr F. Sowerbutts, the Rt. Hon. Lord Erroll of Hale, Mr H. C. Worsdall (member, Exhibition Committee (partly hidden)), Mr A. S. Fraser (Chairman, Exhibition Committee), the Mayor of Haringey, Ald. V. P. Gellay, and Mr R. H. Hamblin (Director & Secretary)

The Twentieth Technical Exhibition was held on 25-29 March 1968 at Alexandra Palace, London. As usual, there was a large interest from overseas countries, as shown by the attendance of representatives from 32 countries: Argentina, Australia, Austria, Belgium, Brazil, Canada, Czechoslovakia, Denmark, Finland, France, Germany, Greece, Holland, India, Ireland, Italy, Japan, Libya, Malaya, New Zealand, Norway, Pakistan, Poland, Portugal, South Africa, Spain, Sudan, Sweden, Switzerland, USA, USSR, West Indies. Total attendance at the exhibition was estimated at over 12,000.

This year there was a further expansion in the exhibition floor space occupied, which was over 27,000 square feet, and there were 108 stands, including exhibitors from ten overseas countries, Belgium, Denmark, Finland, France, Germany, Holland, Italy, Sweden, Switzerland and the United States of America. In addition, products of many other overseas firms were shown on the stands of agents in this country.

Exhibition luncheon

The exhibition luncheon was held on Monday 25 March at the Savoy Hotel, London WC2, and was attended by over 300 members, exhibitors and guests. The principal guest was the Rt. Hon. Lord Erroll of Hale, PC.

The address of welcome was given by the President of the Association, Mr F. Sowerbutts, who referred to objects of the exhibition in aiding the dissemination of the results of research and development. Such an opportunity for social contacts was as important in the technical as in the purely commercial fields. As Chairman of the Technical Exhibition Committee for six years, he was well aware of some criticisms which had been made of the nature of the exhibition. It was the insistence by Council that the high technical content should be maintained which was responsible for the high international repute of the exhibition and the large number of foreign visitors.

Referring to Association matters, he was very pleased that in this jubilee year, Council had re-designated the appointment of the chief executive officer, Mr R. H. Hamblin, as Director & Secretary of the Association. The Oil and Colour Chemists' Association was in a very healthy state, with an exhibition of international repute, a monthly journal of very high standing, biennial conferences attracting delegates from many countries, and an active and enthusiastic membership in sections at home and abroad. Mr Sowerbutts was planning a world trip in the autumn, which would give him the opportunity of visiting members in the new Oil and Colour Chemists' Association, Australia, as well as the Sections in South Africa and New Zealand.

The Council had been particularly interested in the question of the future development of the Association, and had set up working parties in education and training. Mr Sowerbutts also referred to the award in memory of the late Dr Jordan, which was open to all members of the Association under the age of 35, and said that the closing date had now been extended to 1969, and it was hoped that it would be possible to present the successful paper at the next conference.

Mr Sowerbutts then welcomed the guests, especially those from overseas. He extended a welcome to the Presidents of the British Plastics Federation, Mr G. F. Ashford; Institute of Metal Finishing, Mr J. N. T. Adcock; Institute of the Rubber Industry, Mr D. B. Collett; Paint Makers Association, Mr B. Butler; Plastics Institute, Dr W. Blakey; Research Association of British Paint, Colour & Varnish Manufacturers, Mr L. W. Robson; Royal Institute of Chemistry, Mr L. H. Williams; Society of British Printing Ink Manufacturers, Mr R. M. C. Nunneley; Society of Chemical Industry, Mr N. Iliff; Society of Dyers & Colourists, Prof. R. H. Peters; the Vice-President of the Society of Leather Trades Chemists, Dr J. P. Danby; the Chairman of British Colour Makers Association, Mr. J. Smethurst; British Standards Institution, Mr G. H. Beeby; Research Association for the Paper & Board, Printing and Packaging Industries (PIRA), Mr J. A. C. Talbot; Surface Coating Synthetic Resin Manufacturers Association, Mr A. Tremain; and London Section, Oil & Colour Chemists' Association, Mr R. N. Wheeler; the Master of the Worshipful Company of Painter-Stainers, Mr Edward Bush; the Directors of Paintmakers Association, Mr K. S. Flory; (PIRA), Dr G. L. Riddell; and the Mayor of Haringey, Alderman V. P. Gellay, who was one of our own members.

Mr Sowerbutts then welcomed the guest of honour, the Rt. Hon. Lord Erroll of Hale, PC, who had had a distinguished political career, as President of the Board of Trade,

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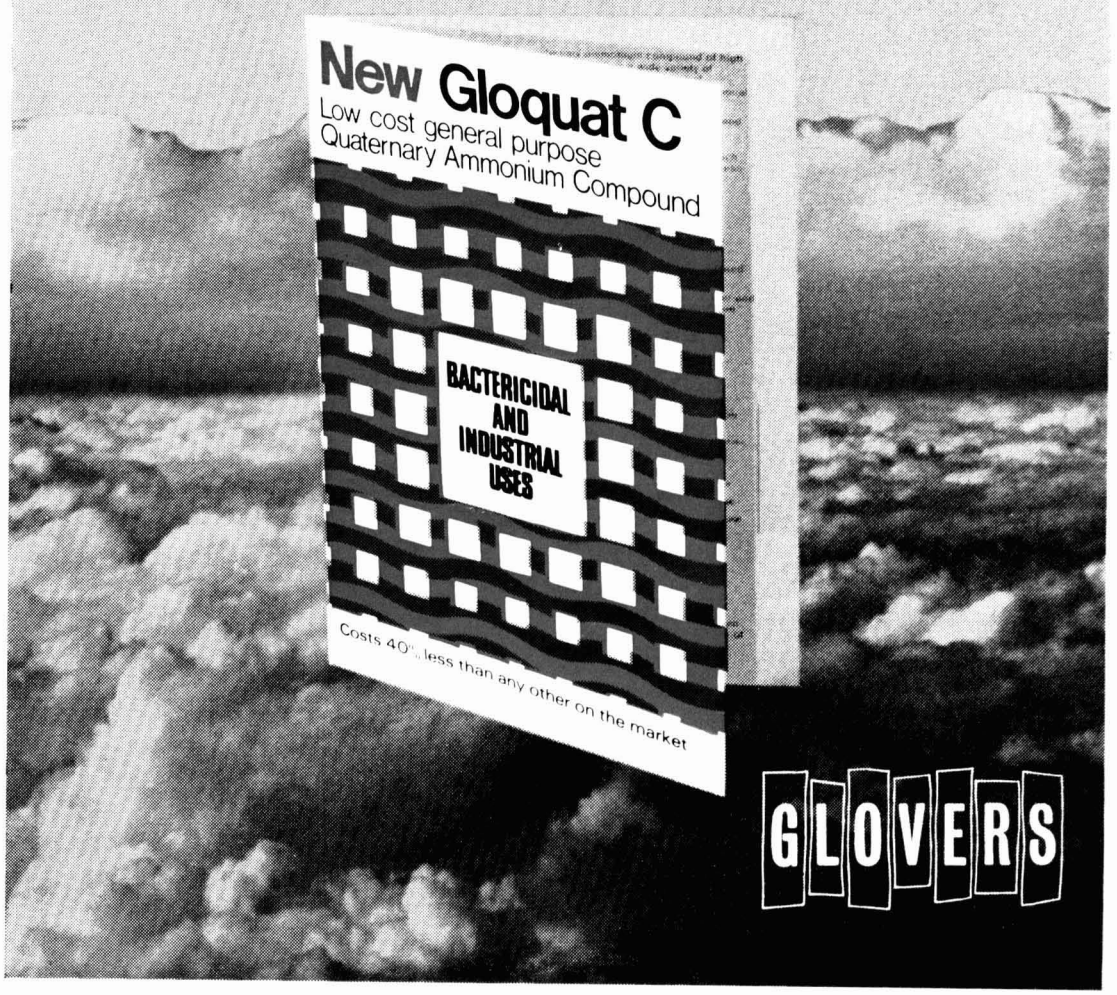
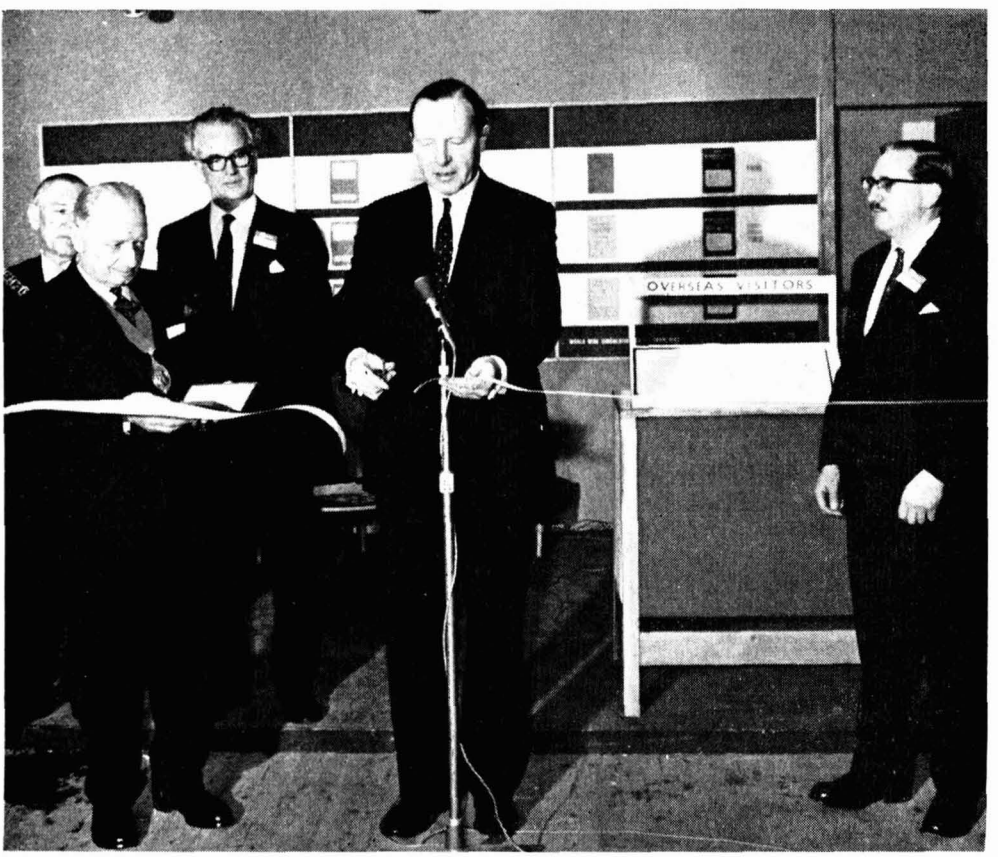


1961-63, Minister of Power, 1963-64, a member of the National Economic Development Council 1962-63, and had also been a member of the Council of the Institute of Directors from 1949-55.

The Rt. Hon. Lord Erroll of Hale, PC, expressed thanks on behalf of all the guests for the opportunity to be present at the opening of an unique exhibition, which concentrated on the demonstration of technical advances and new products. The exhibition had a history of remarkable growth over the last 19 years, starting in 1949 with fourteen exhibits arranged on tables at the Borough Polytechnic. Now there were over 100 stands, representing over 150 companies.

Lord Erroll referred in a very amusing manner to events recorded in the "Times" for 25 March 1949, exactly 19 years ago. Mr Bevin, the Foreign Minister, was sailing to Washington to sign the Atlantic Treaty; 3½ per cent war loan stood at 104; the meat ration was reduced to 10d per week, and banquets, such as the present one, could not exceed 5s 0d per head.

Lord Erroll referred to the jubilee celebrations of the Association to be held in a few months, time, congratulating the Association on 50 years of growth and progress, and concluded by wishing every success to the exhibition.



The traditional cutting of the tape to open the exhibition was carried out by Lord Erroll, watched by (left to right) the Mayor of Haringey, Ald. V. P. Gellay, the President, Mr F. Sowerbutts, Mr A. S. Fraser (Chairman, Exhibition Committee) and Mr R. H. Hamblin (Director & Secretary)

The official opening was performed at Alexandra Palace at 3 p.m. by Lord Erroll, who cut the tape in front of the Association's stand, and afterwards made a tour of the exhibition.

Technical Report

Technical Education

The theme of the Technical Education stand was the history of printing ink technology, which was very well displayed. It was not until 1832 that the first work devoted entirely to printing ink was published by William Savage, who had been a printer to the Royal Institution. There were many interesting facts presented on the development of printing inks, including information on modern methods of production of printing inks with high speed mixing and dispersing equipment. Information was available on further education and training, and one of the suggestions was the new scheme of block release courses. This scheme is at present being offered only by East Ham Technical College, but it is hoped that it will become available at other centres throughout the country.

Once again, parties of sixth-form science students were invited to visit the exhibition, and nearly 250 from 15 schools attended over three days during which short introductory talks were given.

The Technical Education stand had the theme "Historical and technological development of the printing ink industry," and examples of the main printing techniques now in use were shown

Research Associations

The PAINT RESEARCH STATION exhibit was concerned with the newer instrumental analytical techniques now available. Nuclear magnetic resonance spectroscopy provides information about the number of protons present in various structural environments, and the display featured a model of a typical alkyd molecule, with the identification of the bonds in the NMR pattern corresponding to the presence of various groups. Gel permeation chromatography was used to determine the molecular size distribution of polymers by fractionation on a column of graded pore sizes, and typical results for various types of media were shown, together with a model showing very clearly the principles of operation of this technique. The third exhibit was concerned with atomic absorption spectroscopy, which can be used for the determination of trace amounts of metals in paints and pigments.

The Paint Research Station stand featured instrumental methods of analysis

The PAPER and BOARD, PRINTING and PACKAGING INDUSTRIES RESEARCH ASSOCIATION (PIRA) exhibit dealt with instrumental control of printing ink properties. The sources of possible errors in fineness-of-grind gauges were illustrated, and methods of standardisation were shown. The PIRA on-press film thickness monitor was shown, as a prototype model. This is designed to give continuous metering of the inking level. Other displays were of instruments which had been developed for research or quality control, including the well-known *PATRA Tackmeter*.

The BRITISH IRON AND STEEL RESEARCH ASSOCIATION exhibit included information on current research in the use of protective coatings for steel. A flow diagram showed the preparation of blast-cleaned steel strip, and another exhibit was concerned with methods used to obtain a rapid appraisal of the durability of paint films on steel. Also displayed was the *Videlac* process, in which evaporated low molecular weight resins were deposited in a vacuum on a continuously moving strip.

Pigments

ALBRIGHT & WILSON featured the use of zinc phosphate, a white, non-toxic material, as an anti-corrosive pigment for primers. The main applications were in the protection of structural steelwork, in etch primers and in paints for electro-deposition. ALLIED CHEMICAL CORPORATION showed new Harmon perylene pigments, *Indofast Brilliant Scarlet Toners R.6405* and *R.6507*, used in metallic finishes. A new quinacridone red, *Quindo Red R.6730*, was also displayed in metallic finishes, and showed a strong low angle colour. Other quinacridone reds from the range were displayed reduced with white or with red iron oxide. A display of panels after 18 months' Florida exposure indicated the improved lightfastness of lakes of a range of Harmon colours compared with the corresponding toners.

The AMALGAMATED OXIDES exhibit included a study of the performance of zinc silicate paints based on *Zincoli* zinc dust in sodium silicate and a quaternary ammonium silicate. While best results were obtained with the latter, good results were also obtained with mixtures of sodium silicate and quaternary ammonium silicate. In another display, the anti-corrosive properties of a series of zinc-rich paints at 85, 90 and 95wt per cent pigment, extended with aluminium, zinc oxide and calcium carbonate, were studied, and protection was found to be dependent upon the pigment concentration and extender used. There was considerable advantage in the use of zinc oxide as extender. Another exhibit referred to the use of zinc-rich primers for coating steel reinforcing rods for concrete, and these were found still to afford considerable corrosion protection after four years' exposure.

BASF (UNITED KINGDOM) had on display a number of new pigments and developments of existing grades. *Heliogen Blue LBGA* was a beta-form copper phthalocyanine pigment of easy dispersibility, with improved shade and colour strength. A new range of benzidine yellow pigments, *Lithol Yellows 8G, 3G, G, NG, GR* and *4R*, were now available for the first time from BASF. Two members of a new *LV* range of easily dispersible pigments were available, *Lithol Yellow NG-LV10* suitable for toluene gravure inks, and *Heliogen Blue LBGN-LV50* suitable for general applications in inks and paints. Two new pigments for plastics were shown, *PV Yellow 8G* and *PV Fast Yellow 4R*. *Fanal Violet RM* was the first member of a new range of *Fanal M* pigments. In the field of pigment dispersions, *Luconyl Yellow G, Orange RN, Red FGR, Blue LBGO* and *Black N* were new products in a range which has replaced the previous *Colanyl* aqueous dispersions. Pigments dispersed in polyisobutylene now include *Oppasin Fast Yellow GR, Fast Orange G* and *Fast Red B*. *Euviprint Yellow 4R* dispersed in a soluble vinyl chloride/acetate copolymer, and *Euvinyl Yellow 8G* and *4R* in a polyvinyl chloride were for plastics applications. The trade name *Euthylen* has now been adopted for a range of pigments dispersed in polyethylene, for use in

the colouring of polyethylene plastics. An additional feature of the exhibit was a display of panels after Florida exposure tests of a range of pigments in alkyd melamine media.

FARBENFABRIKEN BAYER displayed new grades of titanium dioxide pigments. *Bayertitan RKB3*, a new post-treated grade giving good gloss and freedom from gloss haze, was suitable for automobile finishes. *Bayertitan RD* was a new lower TiO_2 content rutile pigment for emulsion paints, and *Bayertitan AN2* was a new post treated anatase pigment designed for use in stoving finishes for indoor use. A new micronised yellow oxide *3920* had a particularly low oil absorption and new black and brown iron oxides for the building industry, with increased tinting strengths, were on display.

The theme of the BRITISH TITAN PRODUCTS COMPANY exhibit was durability testing, and a comprehensive booklet (BTP/146) was available describing work carried out on natural and accelerated weathering. The display included details of weather records at natural exposure stations throughout the world, and as examples of such evaluation, the performance of pigmented alkyd paints, acrylic automobile finishes, coil-coating enamels of high durability, and a melamine-alkyd enamel were featured. Further information was available on *Tioxide R-XL*, a heavily surface treated rutile pigment developed for emulsion paints, which was first exhibited at last year's exhibition. This consisted of a demonstration of the economy of using a white of high reducing power, rather than a larger amount of a white of lower reducing power, when tinting latex paints.

CIBA CLAYTON displayed the range of *Cromophtal* pigments, including a new product, *Cromophtal Brown 5R*, illustrated in use in an automobile finish.

COLUMBIAN INTERNATIONAL showed their range of carbon blacks, including new versions of *Peerless 155* and *Raven 35* with improved dispersibility. *Dispersil* pigments produced by Runnymede Dispersions, now a part of the Columbian Group, were also shown. DURHAM RAW MATERIALS featured the use of zinc dust and zinc flake pigments in anticorrosive primers. Zinc flake/aluminium pigmented primers with as low as 70 per cent metal in the dry film showed no breakdown after four years' exposure.

GEIGY (UK) showed several new phthalocyanine pigments, including *Irgalite Blue PDS 5*, a beta-form pigment in the *PDS* range of easily dispersible pigments, *Irgalite Blue PR7*, also a beta-form phthalocyanine, for publication rotogravure inks, and *Irgalite Blue LGLD*, a beta-form pigment for letterpress and offset inks. Interest in the potential toxicity of pigments has led to the development of the AT (Analytically Tested) range of pigments for use, e.g., in pencils used for schools, including a new barium-free toner, *Irgalite Red 2BY*. Also on display were the *Irgazin S* series of pigments for use in plastics, e.g., rigid pvc, polystyrene, polyethylene and polypropylene, and *Irgaphor* master-batches for the coloration of rubber.

FARBWERKE HOECHST displayed pigments now available in granulated form, including *Hansa Yellow G 02 gran.* New easily dispersible pigments for air drying paints included *Hansa Yellow G40* and *Hansa Yellow IOG-40*. New developments in the *Permanent H* range included *Permanent Red HF3S*, *Permanent Carmine HF3C* and *HF4R*, and *Permanent Bordeaux HF3R*. These pigments are suitable for high quality printing inks, and their fastness to overspray in stoving paints is particularly valuable. The *Hostaperm* range of high-fastness pigments includes quinacridones and now phthalocyanines, a new development for Hoechst. New pigments especially for printing inks include *Permanent Yellow G* and *G3R* and *Permanent Rubine F6B*, a pigment suitable for multicolour printing according to BS4160 (1967), an easily dispersible benzidine yellow, *Permanent Yellow G 2O*, for publication gravure inks, and *Permanent Yellow GR5O* for letterpress and offset inks were also displayed.

The Association's Information Centre featured displays of the various styles of the journal over the past 50 years, and each of the official guides for the 20 technical exhibitions. Also shown were graphs showing the growth of the exhibition, membership of the Association and circulation of the journal, and a display of the various items approved by Council to commemorate the 50th anniversary of the Association

HARDMAN & HOLDEN showed two new easily dispersible iron blues *Manox Blue MMI* and *MM2* for printing inks. These surface treated pigments have improved ease of dispersion in low polarity media, and low oil absorptions. Also displayed were the DuPont range of *Cinquasia* quinacridone and phthalocyanine pigments, and *Afflair* metallic flake colours.

HUBRON SALES exhibited the ranges of dispersed pigments produced by the California Ink Division of Tenneco Chemicals, including the *Uni-cal 66* range for quick drying industrial finishes, the *Cal-tint* range of closely standardised dispersions for use in both emulsion and solvent-based paints, and the *Colortrend* range for decorative alkyds.

IMPERIAL CHEMICAL INDUSTRIES showed further developments in the *ED* range of easily dispersible pigments. *ED Polymon* pigments designed for use in plastics, now include *ED Polymon Green GN*, a phthalocyanine green, and *ED Polymon Blue LB*, a phthalocyanine blue. While designed specifically for polyolefines, these pigments may also be used to advantage in other polymers, e.g., high impact polystyrene and ABS. The full range of *ED-P* pigments for paints, and *ED-I* pigments for inks now includes a benzidine yellow, *ED-I Monolite Yellow GL*, phthalocyanine green, *EDI Monastral Fast Green GN* and two grades of *ED-P Monolite Fast Yellow VGH* and *VIOGH*, with good stability to heat during dispersion. New developments in conventional pigments include *SS Rhodamine Red 6 GB 500*, for use in flexographic inks and *Rhodamine Lake Red 6 GBX 500* for lake making with, e.g., phosphotungstomolybdic acid. *Fastel Pink B CF* is a new copper ferrocyanide lake of *Rhodamine 6G*.

KINGSLEY & KEITH featured a display of *Sherwin-Williams* alkali blue toners including pigments flushed in litho varnish and a range of synthetic media. A number of items of technical interest were included in the KRONOS TITANIUM PIGMENTS exhibit. The effects of varying pigment volume concentrations were shown with titanium dioxide/extender mixtures in latex paints exposed on an equivalent volume and also an equivalent weight basis, pigmentation being with *Kronos RN 44* and *Kronos RN 56*. The use of wet and flow points to determine the surfactant demand was shown. Also on display were exposure results for up to 20 months, for latex paints based on PVA, polyvinyl propionate, and styrene-butadiene latices. Panels were displayed showing the use of the new chloride process pigment, *Kronos CL 300* compared with the established sulphate process pigment, *Kronos RN 59*. Another new product was a new standard grade, *Kronos RN CX, 68*, with improved dispersibility, with properties close to those of premium grades. Panels showing the results of exposure tests of *Kronos RN 56, RN 57*, and *RNC*, in a number of media were exhibited. A new laboratory technique displayed was the use of small separate black and white tiles as substrates for hiding power tests, which could be used with stoving media. LAPORTE INDUSTRIES provided information in the uses of various grades of titanium dioxide in surface coating applications.

SACHTLEBEN provided information on lithopone and zinc sulphide pigments, and the *Hombitan* range of titanium dioxide pigments manufactured by their associated company *Pigment-Chemie*. These included a new range grade of post-treated rutile pigment, *Hombitan R 710*. This is a grade free of organic treatment, and was developed for high quality weather resistant industrial finishes. SPELTHORNE METALS exhibited anti-corrosive primers based on metallic lead, in a range of media systems. Coated steel specimens submitted to natural weathering showed the good corrosive resistance of primers based on low viscosity alkyd resins with oil lengths of 70-86 per cent. Other exhibits included quick drying primers based on vinyl toluene modified alkyds. With some water soluble media exposure tests showed that protection equivalent to linseed oil based primers could be obtained. Particularly good results were shown using a drying oil, ethylene oxide condensate, a 100 per cent acrylic emulsion, and a water soluble styrene/butadiene copolymer.

The STERLING COLOUR COMPANY exhibit was based on the use of fluorescent pigments for safety purposes, and garments and equipment were shown coated with finishes and inks based on the new range of fluorescent pigments showing improved light stability. The *Sterling S100* range, the *Sterling U100* range incorporating a UV absorber, and the *Sterling S150* range, with outstanding solvent resistance, were shown. The *Sterling M200* range of micronised pigments was developed for use in rotogravure inks.

N. V. TITAANDIOXYDEFABRIEK TIOFINE showed a new surface treated pigment, *Tiofine R50*, developed for use in emulsion paints, together with information in their established range of pigments. VUORIKEMIA OY also introduced two new grades of coated rutile titanium dioxides, *Finntitan RR2* and *RDE*, the latter for water based paints.

Extenders

BERK had information on barytes and talc, and various grades of Kaolin from Georgia Kaolin Company, including *Glomax LL* for use in emulsion paints.

JOSEPH CROSFIELD & SONS demonstrated the use of synthetic silicate extenders, *Neosyl ET*, *Microcal ET*, and *Alusil ET* in emulsion paints based on ethylene/vinyl acetate, vinyl versatate, and acrylic polymers. Partial replacement of the titanium dioxide and talc in a basic formulation could be achieved without loss of opacity.

LAPORTE INDUSTRIES featured the use of the newly developed synthetic clay, *Laponite*, in non-drip thixotropic emulsion paints. SACHTLEBEN AG had information available on their grades of blanc fixe and barytes.

The official party are shown on their tour of the exhibition, on the PIRA stand (left to right) Mr C. C. Mill (PIRA), the Rt. Hon. Lord Erroll of Hale, Ald. V. P. Gellay, Mayor of Haringey, the President, Mr F. Sowerbutts, Mr R. H. Hamblin (Director & Secretary)

Oils

JOHN L. SEATON displayed a wide range of drying oils emphasising particularly the pale colour of their stand oils and a dehydrated castor oil of low viscosity and low hydroxyl value. REX CAMPBELL featured cyclopentadiene modified drying oils indicating the usefulness of *Necomar F 2080* in wood preservative treatments.

Resins—Emulsion polymers

BASF (UNITED KINGDOM) had further technical information on *Acronal 290D*, introduced last year. This is a styrene-acrylate copolymer emulsion with very high pigment binding capacity and suitable for a wide variety of emulsion paints. BRITISH RESIN PRODUCTS featured *Epok V 804/83*, a vinyl acetate copolymer emulsion containing a high proportion of *VeoVa 911* and also a new olefin modified emulsion, *Epok V 8300*.

HARLOW CHEMICAL COMPANY demonstrated the effect of fire on a newly developed intumescent fire retardant paint based on *Mowilith Beta AC 43* and con-

taining *Phoschek P/30*, a nitrogen containing phosphate. This paint, in a two coat application to untreated hardboard and compressed strawboard, upgraded the performance of the substrate from Class 4 to Class 1 rating, when tested according to BS 476. This company also featured an interior masonry finish based on *Revacryl 144* and an exterior textured finish having good adhesion and easy application properties based on *Mowilith DM 21*.

LENNIG CHEMICALS showed a range of paint formulations with different opacity and levels of gloss using their well established acrylic emulsion *Primal AC22*. RESINOUS CHEMICALS demonstrated the flexibility in formulation of paints based on *Wresimul 40400, 40500 and 40600*. A particular feature stressed was the high critical pigment volume concentration possible with these emulsions.

SOCIETE DES USINES CHIMIQUES RHONE-POULENC displayed copolymer emulsions *Rhodopas 5000M* and *5000SMB* and compared the film properties of externally plasticised homopolymers with their copolymers in terms of weathering and water resistance.

A prominent feature of the VINYL PRODUCTS stand was the recently developed ethylene grafted vinyl acetate copolymer emulsion, *Vinamul 6700*. Of particular interest was a display of the methods used for evaluating quantitatively the pigment binding power of emulsions.

POLYVINYL CHEMIE HOLLAND exhibited their range of acrylic polymer emulsions including a styrene/acrylic type newcomer, *Neocryl SR 283*, designed for floor polishes removable with ammonia. It matches the properties of the previously shown *Neocryl SR 280* but at a lower cost.

Resins—water dispersible

CRAY VALLEY PRODUCTS introduced a new water soluble phenolic/alkyd complex, *Resydrol E 452* suitable for primers and designed to meet the requirements of ASTM B-117-64 (hot salt spray test). FARBENFABRIKEN BAYER indicated new fields of application for their recently developed air drying acrylic copolymer dispersion, *Ercusol 1 60*. This was particularly suitable for thick coatings and in joint-filling compositions.

SHELL CHEMICALS UK had further information available on their water soluble *Epikote DX16*, introduced last year for electrodeposition applications. Water soluble alkyds suitable for electrodeposition were shown by DEUTSCHER INNEN- UND AUSSENHANDEL CHEMIE and FARBENFABRIKEN BAYER. The latter company also introduced a new water soluble thermosetting acrylic, *Baycryl W 460*.

KINGSLEY AND KEITH had information on new water dispersible polyamide resins, *Casamid 350* and *351*, produced by THOS. SWAN & COMPANY. SHAWINIGAN exhibited some interesting strippable coatings based on either a latex of polyvinyl butyral, *Butvar BR* or on a solution of a carboxylated polyvinyl acetate resin, *Gelva C5*. The former could be stripped without tearing mechanically whereas the latter could be readily removed by washing with detergent solution (pH = 10).

Resins—polyurethane

BECK, KOLLER demonstrated new outlets for standard resins as exemplified by the use of a moisture-curing polyurethane, *Beckurane M 330*, in seamless coloured flake flooring compositions. Advances in resin technology included the development of a thixotropic urethane oil, *Beckurane 400*, while attention was drawn to the good colour retention shown by certain moisture curing (*Beckurane M-181 and M-191*), two-pack (*Beckurane 2-299*) and urethane oil (*Beckurane 72-70*) type media.

CRAY VALLEY PRODUCTS featured new urethane polymers, *Unithane 651 W* and *Unithane 652 W*, having thixotropic properties. These products offered interesting

Over 12,000 people are estimated to have attended the Exhibition, and good use was made of the seating area in front of the Information Centre

possibilities for high build airless spray coatings for steel structures. FARBENFABRIKEN BAYER introduced a new mixed aliphatic/aromatic polyisocyanate, *Desmodur HL*, for two-pack polyurethanes, and also a hexamethylene diisocyanate adduct, *Desmodur N 75*, for use in upgrading nitrocellulose. SCADO ARCHER DANIELS featured two new air drying urethane vehicles, *Arothane 181-ML-60* based on linseed oil, and *Arothane 190-ML-50* based on a safflower alkyd.

IMPERIAL CHEMICAL INDUSTRIES demonstrated the use of *Daltolac 2170* and *1140* in flooring compositions. Large floor panels were exhibited which gave an

attractive multicoloured effect achieved by the inclusion of coloured chips in the lacquers. POLYVINYL CHEMIE HOLLAND showed a recently introduced one-pack, oil free, moisture curing polyurethane, *Neorez U 105* having fast drying and excellent hold out properties.

Resins—epoxy

CIBA (ARL) introduced a new epoxy resin, *Araldite 7300*, particularly suitable for use with cheaper solvent blends. Displays included the effect of choice of epoxy resin and type of hardener in epoxy-coal tar compositions on recoating times and corrosion resistance, and the behaviour of one pack prefabrication primers on salt spray exposure.

DOW CHEMICAL exhibited a range of epoxy resins suitable for the preparation of esters having good pigment wetting properties and giving films of high gloss. Also shown were the latest developments in powder coatings based on epoxy resins or epoxy-Novalac systems aimed at high reactivity and improved edge coverage.

SHELL CHEMICALS UK featured the uses of *Epikote* resins in high solids and solventless paint for application by heated two-component spray equipment. New curing agents for these systems were *DX 103* (for temperatures down to 0°C) and *DX 104* (for temperatures down to 8°C). A ketimine type curing agent *H3* could also be used giving adequate pot life in one pack systems.

ANCHOR CHEMICAL COMPANY showed their extensive range of epoxy resin curing agents, including *Ancamine LT* which will cure at −5°C and is also effective under water, *Ancamide 400* for use in epoxy flooring compositions and solventless coatings and the BF_3 complexes, *Anchor 1170* and *1222*, characterised by a long pot life.

Resins—acrylic

BRITISH RESIN PRODUCTS showed an acrylamide type resin, *Epok D1172*, embodying new polymer modifications giving good flow and freedom from surface defects. A particularly interesting exhibit illustrated recent research into the viscosity characteristics required for bake-sand-bake finishes. Flow curves, in conjunction with electron micrographs and test panels, showed the desirability of avoiding pigment flocculation. The results were related to the development of coatings based on a thermosetting hydroxylated acrylic resin, *Epok D210/149*, showing excellent reflow properties and capable of accepting overspray.

CRAY VALLEY PRODUCTS featured *Synocryl 823S* for use in thermosetting finishes at relatively low cost. An interesting newcomer was *Synocryl 865S* which may be cross-linked with aliphatic or aromatic diisocyanates at room temperature to produce coatings of excellent chemical resistance and flexibility. SYNTHESE, KUNSTHARSFABRIEK showed recent developments in reflow thermosetting acrylic systems with emphasis on the use of *Setalux C1140 BX-51* in conjunction with a melamine resin. Demonstration panels indicated the improvement in film appearance obtained by initial curing at 80°C, sanding, and then reflowing for 12min at 140°C.

LENNIG CHEMICALS featured two thermosetting acrylics, *Paraloid AT-71* and *AT-75* and their use for interior coatings of food containers was demonstrated. Also shown was a new air drying acrylic resin. *Paraloid B48*, for single coat finishes on metal. KINGSLEY & KEITH showed three new thermoplastic acrylic resins, *Pontybonds 4420*, *4400* and *4500*, manufactured by the PONTYCLUN CHEMICAL COMPANY. These resins had been specially designed for use in liquid printing inks and overprinting lacquers, being characterised by very low odour, high gloss and excellent compatibility with nitrocellulose.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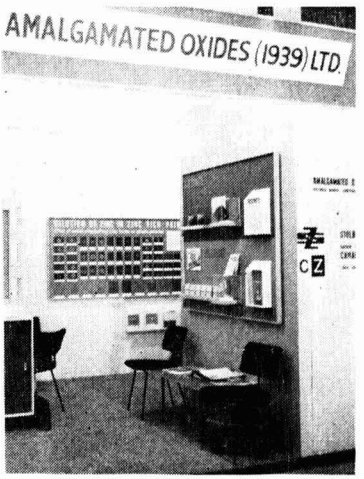
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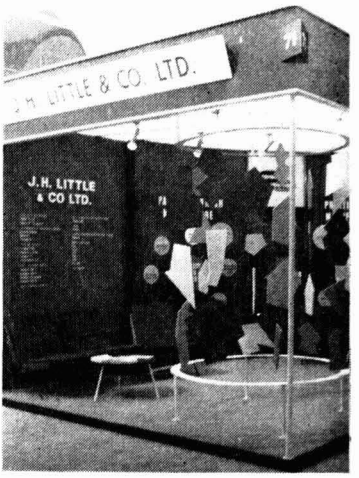
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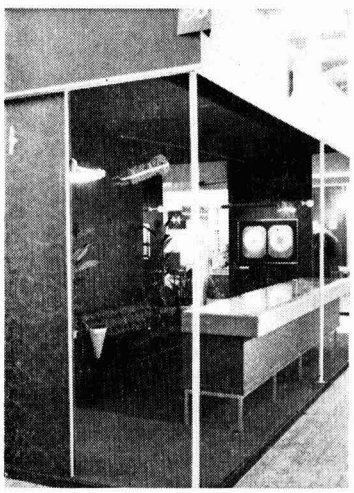

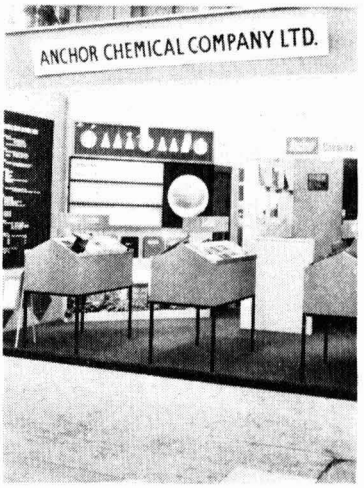
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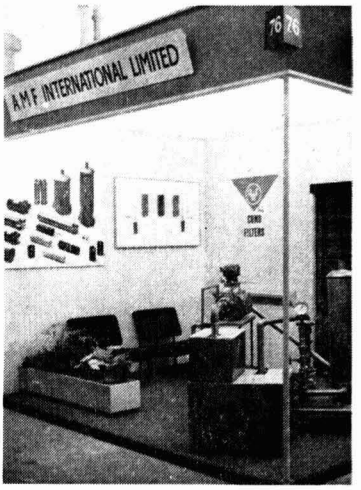
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SPELTHORNE METALS LIMITED
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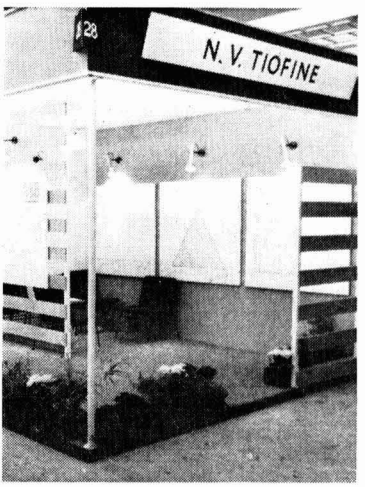
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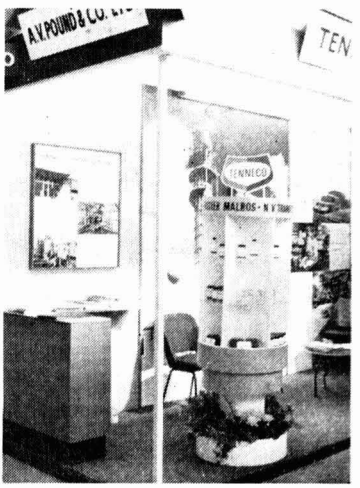

TENNECO

UNION CARBIDE EUROPE introduced a new thermoplastic resin *Acrylic 405*, having a wide range of compatibility with other resins. In particular this resin showed a very high impact resistance and was recommended for use in sandable topcoats or sealers for wood.

Resins—alkyd (drying oil modified)

SCADO ARCHER DANIELS showed a recently developed medium oil alkyd, *Scadonal 48*, which had been specially designed for rapid drying automotive repair enamels. SHAWINIGAN had an interesting selection of chromatograms obtained by gel permeation chromatography and illustrating the effect of cooking procedure and composition of pentaerythritol alkyds on their molecular weight distribution. This was related to certain film properties such as drying time etc.

BECK, KOLLER had information on a recently developed thixotropic alkyd, *Beckogel 1488*. A new safflower type alkyd, *Alkydal U60*, available in low or high viscosity grades was shown by FARBENFABRIKEN BAYER. J. H. LITTLE had information available on the *Lioptal* range of alkyd resins produced by HENKEL INTERNATIONAL for use in various types of printing inks. SVENSKA OLJESLAGERI AKTIEBOLAGET introduced new air drying alkyds, including *Soalkyd 3123*, a safflower type of good brushing characteristics and *Soalkyd 3947*, a linoleic type of good colour retention and suitable for spray application.

Resins—alkyd (plasticising)

BRITISH RESIN PRODUCTS exhibited for the first time oil-free polyesters *Epok A5000/60* and *A5001/60*. These polyesters in combination with a suitable melamine resin may be used for coil coating applications where good colour retention is essential. Another interesting newcomer was an acrylated alkyd copolymer, *Epok A6005/50*, specially designed for use with melamine resins for general automotive and domestic appliance applications.

CHEMISCHE WERKE HUELS showed newly developed saturated hydroxylic polyesters, *BL 901* and *904*, for use with melamine resins in car finishes. SCADO ARCHER DANIELS also introduced a new oil free alkyd or polyester type resin, *Scadonal 220*, for the formulation of stoving enamels having high alkali and detergent resistance in non-yellowing finishes.

SYNTHESE, KUNSTHARSFABRIEK extended their range of oil free alkyds with *Setal 175 XX-60* for use in a number of applications including automobile stoving enamels, acid curing finishes and NC lacquers.

SVENSKA OLJESLAGERI AKTIEBOLAGET showed a recently developed versatic acid modified alkyd, *Soalkyd 4496*, for use in stoving enamels in combination with melamine or thermosetting acrylic resins. New development products included an experimental alkyd *F 9000* of the oil free type for stoving finishes, and *F 9135*, based on branched chain acids for stoving and cold curing finishes.

Resins—amino

BIP CHEMICALS featured a new high solids low viscosity melamine resin, *Beetle L3181*, having exceptionally good compatibility with thermosetting acrylics and being particularly suitable for use in bake-sand-bake finishing of automobiles and domestic appliances. FREDK. BOEHM had further information available on their highly reactive melamine resin, *Pioneer PF 3*, in low temperature stoving enamels and on *Pioneer FM 544* in precatalysed wood finish formulations. SCADO ARCHER DANIELS showed a new highly reactive melamine resin, *Scadomex 380*, for use in alkyd/melamine finishes for stoving in the range 70-90C. SVENSKA OLJESLAGERI AKTIEBOLAGET introduced new butylated U/F resins, *Soamin 848* and *848 EB*, particularly low in free formaldehyde content.

Resins—polyamide

On the KINGSLEY AND KEITH stand new polyamide resins, *Mykon 528S* and *530S*, were exhibited by the WARWICK CHEMICAL COMPANY. These new grades were complementary to the well established *Mykon 526S* and were designed for use in flexographic inks. CHEMISCHE WERKE HUELS had information on a C_{12} polyamide, *Vestamid*, for use in fluidised bed coatings, flame and electrostatic spraying processes.

Resins—unsaturated polyesters

CHEMISCHE WERKE HUELS exhibited a new air drying wax free polyester, *Vestopal*, for use in fillers and stoppers for repair work. A film of this material cured by electron beam radiation was also shown. FARBENFABRIKEN BAYER showed several new types of polyester resins. A very informative exhibit concerned the use of *Roskydal UV10*, a wax containing polyester specially formulated for one-component lacquers which can be cured by ultra-violet light in less than two minutes. A model showed how this type of curing technique could be readily adapted to production line operation for the application of glossy or semi-gloss clear coatings on wood. Other new products included *Roskydal 501*, a wax free polyester with very rapid drying characteristics, and *Roskydal W13*, a wax containing polyester for use in furniture finishes where quick drying schedules were required.

Resins—miscellaneous

ANCHOR CHEMICAL COMPANY exhibited the *Marbon* range of styrene and vinyl toluene-butadiene resins, including *Marbon 1100T* for use in low odour multi-colour finishes. BASF UNITED KINGDOM showed a new alcohol soluble styrene/maleate resin, *Suprapal AP*, for use in printing inks. This material is almost odourless and can be used on food wrappings. CHEMISCHE WERKE HUELS had on display a range of speciality products, including the *Vilit* series of vinyl chloride type terpolymers, *Synthetic Resins AP* and *RK* (acetophenone-formaldehyde type) for use in NC lacquers and a new low viscosity 1, 4 cis-polybutadiene oil with fast drying properties.

CORNBROOK RESIN COMPANY showed latest developments in their *Printex* range of maleic adduct resins for use in various types of printing inks. Information was also available on new products of the oil reactive phenolic resin type. DEUTSCHER INNEN-UND AUSSENHANDEL CHEMIE also had technical data available on their range of phenolic and maleic type resins.

FREDK. BOEHM had further information on two resinates, *Pioneer R106* and *R107*, introduced last year for use in gravure inks. A new modified phenolic resin, *Pioneer RP6*, specially developed for offset litho inks, and a new isophthalic alkyd, *Pioneer RA4*, for use in offset and heat-set litho inks were also shown.

FARBWERKE HOECHST displayed a recently developed chlorinated polypropylene resin, *Hostaflex PP66*, particularly suitable for use in chemical resistant coatings. IMPERIAL CHEMICAL INDUSTRIES demonstrated their recent studies on the formulation and manufacture of high build chlorinated rubber paints and gave examples of the use of *Alloprene R10* in one coat masonry finishes of outstanding weathering properties.

HUBRON SALES indicated new applications for the *Pliolite* range of resins, including the use of *Pliolite VTAC*, an acrylic/vinyl toluene/butadiene solution resin, in the production of fleck and masonry finishes. The excellent adhesion of this type of coating on powdery surfaces was demonstrated.

KINGSLEY AND KEITH had information available on *Dalvor 720*, a new polyvinyl fluoride resin, for use in coatings on metal appliances. SOCIETE DES

USINES CHIMIQUES RHONE-POULENC featured the use of a polyvinyl formal, *Rhovinal F*, in wire enamels and a polyvinyl butyral, *Rhovinal B*, in etch primers. SHAWINIGAN demonstrated the use of *Butvar* shellac ester in an improved sanding sealer.

TENNECO CHEMICALS featured their range of *Nirez* polyterpene and terpene phenol resins, the main applications being in paper coatings, printing inks and adhesives. A new modified terpene resin, *Nirez X2092*, had been developed for use in neoprene based adhesives to give improved ageing properties.

UNION CARBIDE EUROPE demonstrated the toughness, chemical resistance and adhesion of wash primers and zinc rich primers based on phenoxy resins, *PKHH/C*.

POLYVINYL CHEMIE HOLLAND showed recent developments in their range of acrylic bead polymers and included a new product, *Neocryl B-723*, for use in coil coatings and to improve the petrol resistance of repair lacquers.

Chemical intermediates

BP CHEMICALS (UK) featured a number of new products including ethylene amines and propylene oxide with information on their general uses. The company's range of *Bisomer* monomers was also shown together with data on the effect of hexylene glycol and dibutyl phthalate on the bond strength of a vinyl acetate homopolymer emulsion.

IMPERIAL CHEMICAL INDUSTRIES showed details of studies on the homopolymerisation of vinyl acetate. Investigations had also been carried out by a radioactive tracer technique to follow the migration of a labelled anionic surfactant to the surface of the film and this had been related to the loss of water sensitivity. The TROJAN POWDER COMPANY exhibiting on the KINGSLEY & KEITH stand had their latest information on the use of *Trimet* (trimethylol ethane) and *DMPA* (dimethylol propionic acid) in resin manufacture.

NOVADEL featured the use of *Nouryset* intermediates in thermosetting acrylics, polyurethane lacquers and water soluble acrylic resins. Also demonstrated was the use of the vinyl ester of *Siccatolic* acid as a modifying monomer for vinyl acetate emulsions.

SHELL CHEMICALS (UK) demonstrated the use of Versatic acid in two main applications: (I) in the form of its vinyl ester as comonomer with vinyl acetate or vinyl chloride in emulsion systems and (ii) as the glycidyl ester for use in alkyd formulations. Examples of the latter use included the development of a new low bake DCO alkyd with improved adhesion, stain and petroleum resistance and a water soluble alkyd, *DX 27*, suitable for electrodeposition.

TENNECO CHEMICALS featured a range of rosin derivatives including *Nilox* disproportioned rosins of outstanding resistance to oxidation. UNION CARBIDE EUROPE introduced a new alkyd resin intermediate, *Polycyclol 1222*. This material is an epoxy alcohol with a saturated ring structure and imparts excellent alkali and chemical resistance.

AMOCO CHEMICALS had the latest information on uses for trimellitic anhydride which is shortly going into full scale production. Details on the preparation of resins based on trimellitic anhydride and suitable for the electrodeposition of primers or single finishing coats were available.

Solvents

BP CHEMICALS showed their *Bisol* range of solvents. A display featured recent studies of the solubility of polyvinylidene chloride resins in a number of single solvents and binary mixtures. While tetrahydrofuran was an excellent solvent for polymers

with a vinylidine chloride content >92 per cent, acetone has been shown to be a promising diluent, having several advantages over the commonly used toluene.

CARLESS CAPEL & LEONARD showed technical heptane and hexane with normal paraffin contents >90 per cent. Special fractions with closely controlled contents of *n*-paraffins, naphthenes and aromatics were being developed. REX CAMPBELL & COMPANY provided information on their range of ester solvents, and odour-free grades of *Magie* distillates of US origin. CHEMISCHE WERKE HUELS showed two new products, isobutanol and a lacquer grade trichlorethylene.

In the ESSO CHEMICALS display, emphasis was placed on the new plant being brought into operation this summer at Fawley, with a capacity of 290,000 tons aromatics. The range of solvents available has been extended and now includes SBP solvents with very low benzene contents.

SHELL CHEMICALS (UK) provided information on their extensive range of solvents including solution viscosity data for acetone, MEK and MIBK, water miscibility, blush resistance and solution viscosity data for high boiling ketones, and the properties and uses of a range of glycol ethers.

Plasticisers

BP CHEMICALS provided information on toxicological properties, including BPF ratings and FDA acceptances, of the *Bisoflex* range of plasticisers. REX CAMPBELL showed the use of tritolyl phosphate in promoting fire retardance. Information was also provided on the use of diamylphthalate. TENNECO CHEMICALS showed an extensive range of alkyl and aryl phosphates produced by Butler Chemicals, including tributoxyethyl phosphate and trioctyl phosphate.

Additives, driers, fungicides, surfactants etc.

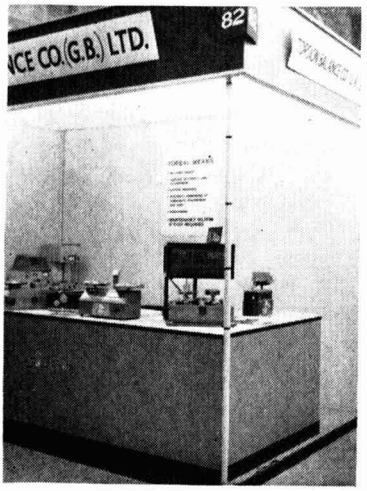
ALBRIGHT & WILSON showed organotin compounds as fungicides for emulsion paints and marine anti-fouling compositions, including tributyltin oxide and a new product, tributyltin fluoride. ALLIED CHEMICAL CORPORATION showed the use of low molecular weight polyethylene as a flatting agent in NC lacquers, as an additive for improving the rub-resistance of printing inks, and as a film toughener for traffic paints. BAKER CASTOR OIL COMPANY provided information on their range of *Thixacin R*, *Thixatrol ST* and *MPA* and *Post R* additives for control of rheology, thixolotropy and pigment suspension.

BERK provided information on the use of *Bentone 11N* in paints for electro-deposition, and other thixotropic agents in various types of system. A new application was the use of *Bentones* in lithographic inks to control flow, pigment packing and colour development, and in newsprint inks to aid in overcoming the problem of misting with high speed rotary presses. *Flammex 5BT*, a pentabromotoluene fire retardant, can be incorporated into emulsion paints without loss of desirable properties. BRITISH CELANESE showed various uses of water soluble cellulose ethers in emulsion paints.

BUSH, BEACH & SEGNER BAYLEY showed the use of BASF polyethylene waxes as matting agents for lacquers and for imparting rub-resistance to printing inks. REX CAMPBELL showed an improved grade of cuprous oxide for anti-fouling compositions, *Ceresperse* water dispersible high melting point waxes, *Glyconol*, a new gellant and viscosity modifier, the new *Glycox* range of octyl polyethylene polyol nonionic surface agents, and *Crexate M*, a cationic dispersant.

JOSEPH CROSFIELD featured the use of fine particle silicas, *Neosyl ET* and *Gasil MSG 23* and *937*, as matting agents for solvent based paints. The degree of mattness, from satin to full matt, can be controlled by variations in the level of addition. DOW CHEMICAL COMPANY showed a new methyl hydroxypropyl


WINKWORTH MACHINERY


NCE CO.(G.B.) LTD.
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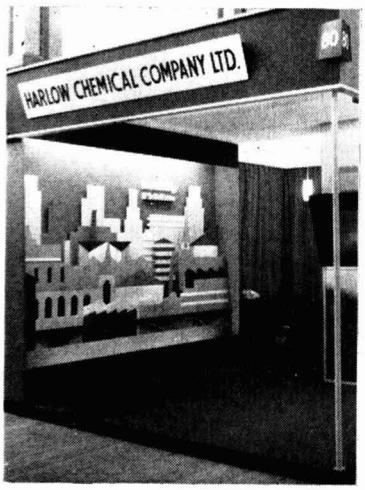
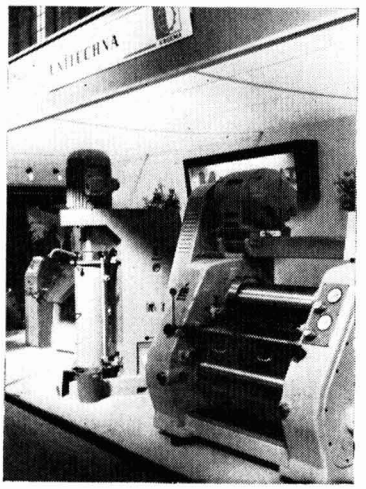
RESINOUS CHEMICALS

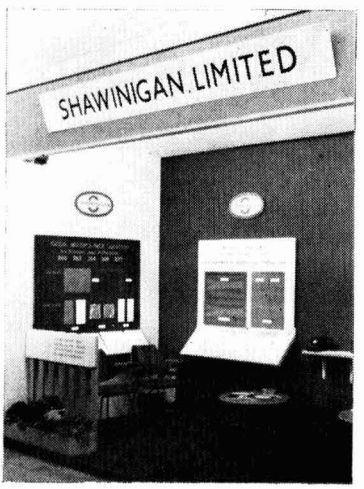

HARLOW CHEMICAL COMPANY LTD.


MENTS LTD.
SHEEN INSTRUMENTS LTD.
SHEEN




BECK, KOLLER & CO. (ENGLAND) LTD.


VUORIKEMIA OY
FINNTITAN
FINNTITAN


SHAWINIGAN LIMITED

cellulose, *Methocel SA 12145*, with easy dispersibility in cold water, for use in emulsion paints. *Dowicil 100* is a new non-phenolic preservative for water based systems, which may be used in place of mercurials. DURHAM RAW MATERIALS provided information on the *Nuodex* range of fungicides.

HARDMAN & HOLDEN featured the use of *Zircomplex PA* and *PN* as additives for thixotropic emulsion paints, and the range of *Manosec* and *Cozirc* driers. J. H. LITTLE showed the well-known anti-settling agents, thixotropic agents, and anti-floating agents etc. from Henkel International. *Dehysol R* is a new liquid product for imparting thixotropy and counteracting flooding and flotation, and can be added to finished formulations or at any stage during manufacture. MODO PRODUCTS (CHEMICALS) showed *Modocoll FQ*, with controlled solubility through a range of pH. A detailed study had been made of the rheological properties of latex paints using *Modocoll E* as thickener. The *Berol* range of surface agents were also presented at the exhibition for the first time.

NOVADEL showed newly developed drier systems based on *Barium Siccatol*, and a barium based composite drier, *Noury Drier 10*, free of lead and calcium. Two new fungicides were shown, *Synox ABF* for chlorinated rubber paints, and *Onyxide 172* for emulsion paints. PURE CHEMICALS, which has now become a subsidiary of the Noury van der Lande group, introduced a number of organo-lead compounds for use as biocides, including hexaphenyl dilead and triphenyllead acetate. These compounds have shown considerable promise in anti-fouling compositions. Also on show were various organotin compounds for use in anti-fouling compositions, and as preservatives for emulsion paints and solvent based paints. Organic phosphorus compounds were also exhibited. *Phosclere T36*, triphenyl phosphite, may be used as an antioxidant, flame retardant, and stabiliser for plastics, and also as a reactive diluent for epoxy resins. BERD SCHWEGMANN KG showed a wide range of additives for viscosity control, anti-foam, and anti-corrosive use, and *Ink Gel S-202* for printing inks.

TITANIUM INTERMEDIATES showed the use of alkanolamine titanates in the production of thixotropic emulsion paints. The alkanolamine titanates are effective for the purpose without the need for pH adjustments. A second display demonstrated the use of aluminium pigmented paints based on the lower titanium alkoxides as heat resistant coatings suitable for use up to 650°C. The organic groups are eventually pyrolysed, leaving behind an adherent matrix of TiO_2 and aluminium.

Instruments

CHURCHILL INSTRUMENT COMPANY exhibited the *Churchill/Metal Box Tackmeter Mark IIIB* with extended speed range which is now available with recorder output. Also on show was the *Churchill Falling Rod Viscometer*, with an automatic digital timer. DE LA RUE FRIGISTOR featured the *De La Rue Climatest* apparatus for accelerated weathering, which incorporates fluorescent lamps combined with temperature and humidity control. DIAF A/S exhibited the *Laray-Tackmeter Type 76B*, for measuring the tack of letterpress and offset inks.

ELCOMETER INSTRUMENTS showed a selection of their established range of instruments for paint testing. A new development was an abrasion tester in which silicon carbide grit was blown on to the test panel. FERRANTI showed their well-known co-axial cylinder and *Ferranti-Shirley* viscometers. JOYCE LOEBL & COMPANY showed the *Colorcord Mark IIA and IIB*. The latter instrument incorporates an additional facility for taking abridged spectrophotometric data by means of 16 narrow-band interference filters. Also on show was the *ICI-Joyce Loebl Disc Centrifuge* for particle size analysis.

KOLLMORGEN (UK) showed a range of equipment for colour measurement, including the *Colour Eye* and the *Colour Analysis Display Computer*. RUDOLPH

MEYERS INCORPORATED showed the *Tack-o-Scope* for tack measurement of printing inks, and the *IGT Printability Tester* which can be set for printing at constant or accelerating speeds.

MICROSCAL showed the *Microscal Flow Calorimeter Mark II* incorporating a DC amplifier, which can be used for the study of interactions between pigments and solutions of media components, including an examination of desorption and displacement phenomena. PRETEMA exhibited the *Pretema Spectromat FS3A*, a newly developed spectrophotometer with 33 narrow band interference filters and a built in tristimulus integrator. Also on show was the digital *Pretema Color Computer.*

RESEARCH EQUIPMENT (LONDON) had on display a selection from their comprehensive range of paint testing equipment. A new item was the *ICI Cone and Plate Viscometer*, which was now available in two ranges, of up to 10 poise at 10,000 sec^{-1} or 20 poise at 2,500 sec^{-1}. Also on show was a new programmer unit for the *ICI Micro-Indentation Apparatus*, by means of which set programmes of application and removal of the load after a prescribed time could be performed.

SHEEN INSTRUMENTS (SALES) showed their extensive range of instruments for paint testing, including the *ICI Gel Strength Tester*, and the *ICI Drying Time Recorder*, and a range of *ICI Rotothinners* to measure up to 340 poise. Also on show were a modified design of the *ICI Film Spinner*, incorporating a revolution pre-setting device, the *Pendulum Hardness Tester* with an automatic counting device, and a re-designed *Falling Block Impact Tester.* THE TINTOMETER LIMITED displayed their range of colour measurement instruments, including the new *Lovibond Flexible Optics Tintometer*, which is a visual colorimeter fitted with a movable viewing head made possible by the use of glass fibre optical components.

Laboratory Equipment

WILLIAM BOULTON showed a range of equipment designed for small batch production and laboratory use. D. H. INDUSTRIES showed several very interesting exhibits, including a water-jacketed laboratory sand mill, and a *Hockmeyer* variable speed mixer with hydraulic lift. A laboratory rig for filling aerosols was shown, including the use of a transparent container to enable the compatibility and stability of aerosol systems to be examined. Also featured was a 60 litre capacity complete resin plant, capable of being used for the solvent or fusion process.

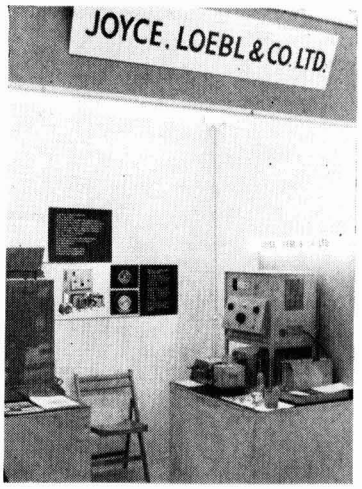
DIAF A/S showed a laboratory *Rota-Flow Mill Type 56T*, a combined dissolver and bead mixing mill, with variable speed (500-3,500rpm). Using a 2-litre sand/bead dispersion container the machine can be used for continuous operation. JENAG EQUIPMENT showed the *Mini Jenag* strainer, designed for laboratory and small batch use.

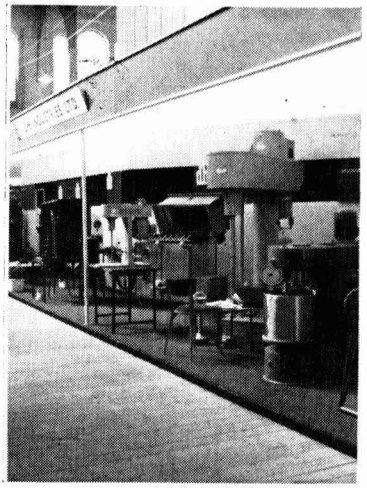
The MASTERMIX ENGINEERING COMPANY exhibit included the *Mastermix 1HP Dissolver*, specifically designed for laboratory and development work. This can be used with heavy pigment dispersions in quantities ranging from half pint to one gallon, and can also be used as a mixer for quantities of up to five gallons. The *Mastermix Mark II Portable Mixer* was also shown. MOLTENI OFF. MECC. showed a laboratory continuous grinder, operating with *Microsfera* ballotini, which has the same features as larger production grinders, and is fitted with an infinitely variable feed pump.

The TORSION BALANCE COMPANY showed a new single pan torsion balance, with full digital read-out, covering the range up to 160g, as well as their existing range of torsion balances.

Manufacturing equipment

AMF INTERNATIONAL exhibited a new trolley-mounted pump filtering and batching unit, by means of which paint is pumped through the *Micro-Klean* cartridges


JOYCE. LOEBL & CO. LTD.




FREDK. BOEHM LTD
FREDK BOEHM LIMITED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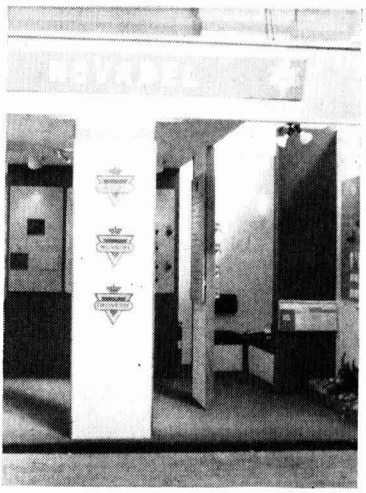
SYNTHESE N.V.




HYGROTHERM ENGINEERING


TORRANCE & SONS LTD.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TITANIUM PIGMENTS LTD.


90
LTD.

in the *Cuno* filter, and then metered directly into drums or tins. Also on show was a heavy duty filter cartridge suitable for coarse grind paints and high viscosity materials. WILLIAM BOULTON showed the *Boulton Vibro-Energy Paint and Ink Strainer* now fitted with a high speed motor and the well known *Vibro Energy Mill* and the *Boulton Hi-Speed Dissolver.*

COX'S MACHINERY showed the *Cox Type 321 high speed Triple Roller Mill,* giving high production without loss of versatility or ease of cleaning. DH INDUSTRIES exhibited a wide range of equipment from their overseas associates. The *Kupper Heavy Duty Kneader*, with a worm extrusion discharge, can be operated under vacuum, and special features include ease of access and safety devices. A new *Sussmeyer Sealed Sand Mill* enables very viscous or thixotropic systems to be processed; an applied pressure keeps the bearings free from paint. A number of other types of equipment were on show including filling equipment.

DEUTSCHER INNEN-UND AUSSENHANDEL CHEMIE had information about a process for continuous production of paints, developed by the Institut für Lacke und Farben at Magdeburg, in East Germany. In the process the raw materials are fed into a sand-milling system, and the concentration of pigment in the dispersion is continuously monitored by means of a radioisotope beta-back scatter system. It is understood that the process is in actual operation. DIAF A/S had information about the range of dissolvers and mixers produced, together with triple roll mills, filling machines, etc. The *Diafill Automatic Filling Machine* was on show; this is adjustable from $\frac{1}{16}$ litre to 12 litres.

DRAISWERKE exhibited the *Drais-Hurricane Rapid Mixer, Type HUK 10,* the *Drais Torrmat* vacuum planetary mixer-kneader, a paste mixer suitable for vacuum operation, and the *Drais Perl Mill Types PM25* and *PM1.* DURHAM RAW MATERIALS showed the *Morehouse International Cowles Dissolver Model 520 VHV,* fitted with a self-contained electric hydraulic pump, and the new *Morehouse-Cowles Sandmill*, which operates at slightly above atmospheric pressure, and eliminates air entrapment and solvent evaporation. HYGROTHERM showed heating systems. JENAG EQUIPMENT showed a new *Mini Jenag* strainer, for small batch use, and other models. MARCHANT BROTHERS showed a range of triple roll mills, and products from MASCHINENFABRIK HEIDENAU in East Germany. A new machine was the *Heidenau Power Grinder 192B*, in which the grinding media consist of toughened silica spheres, and a feature of the machine is the detachable grinding shell, which can be reversed to change the position of maximum wear.

MASTERMIX ENGINEERING COMPANY exhibited some of their range of high speed dispersion equipment, including the *Mastermix VEH Disperser*, the *Mastermix Heavy Duty Paste Mixer Disperser* and a new *Mastermix 1HP Dissolver*, designed for laboratory and development work. DR MEAZZI exhibited their *Vibrofiltro* vibrating screens, and a self-priming diaphragm pump. METAL PROPELLERS LIMITED showed some of their latest developments in heat transfer equipment, resin plant design and fabricating techniques. MOLTENI OFF. MECC. showed a range of mixing and grinding equipment, including mixer-dispersers, planetary mixers, and continuous grinders. PLASTMASCHINENWERK FREITAL exhibited the *Kreisel Turbo-Mixer MKV 160*, with a pressure and vacuum-tight mixing vessel. PETER SILVER & SONS showed a range of mixers, including the *Supershear* machine, which is suitable for viscous liquids with high solids contents. SILVERSON MACHINES showed their range of mixer-emulsifiers, including a new 50hp unit fitted with a multi-shearing head. A *Flash Mix Unit* was shown which dispenses with the need for a pre-mixing stage.

HERBERT SMITH & COMPANY showed a new design of the *Vortexion* high speed disperser-mixer. TORRANCE & SONS showed a new 25hp hydraulically-driven paste mixer, giving very high torque at low speeds. Also shown was an improved


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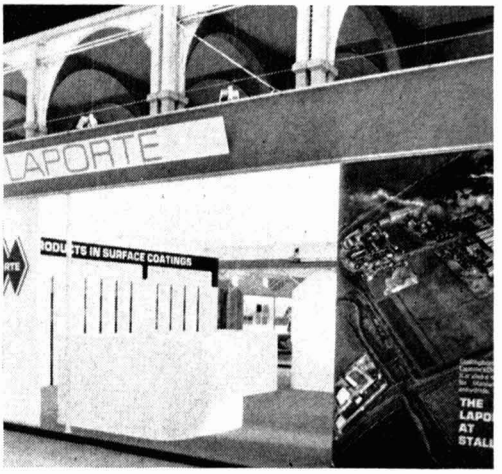
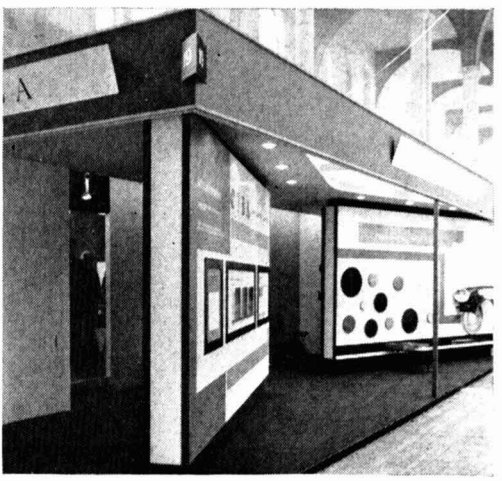
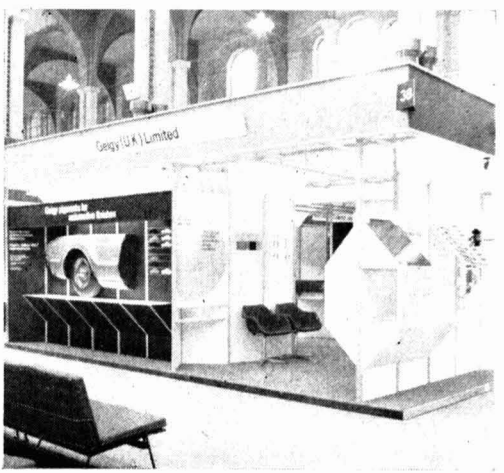
SOCIETE DES USINES CHIMIQUES
RHONE-POULENC


LAPORTE
IN SURFACE COATINGS


British Titan Products Co Ltd
52




CROSFIELD & SONS LIMITED
54
JOSEPH CROSFIELD & SONS LIMITED
Crosfield
The Crosfield Range of chemicals for the surface coating industry
Microcal ET
Alusil ET
Neosyl ET
Gasil
Crestanol
Crestlin


Geigy (U.K.) Limited

range of *Microflow* mills for the production of liquid inks. WINKWORTH MACHINERY showed their new range of horizontal U-trough mixers for powders, a 10 gallon change-pan mixer, and a range of Z-blade heavy duty mixers.

Acknowledgments

The Honorary Editor is indebted to the following members of the Association, who gave so much of their time to assist in the reporting of the exhibition:

H. Archer, R. McD. Barrett, T. R. Bullett, A. E. Claxton, W. M. Collie, F. M. Couchman, W. B. Curtis, R. N. Faulkner, H. Foster, J. R. Green, D. W. Guest, H. R. Hamburg, G. L. Holbrow, V. F. Jenkins, C. H. Morris, R. H. E. Munn, T. D. Nation, L. A. O'Neill, J. R. Pooley, T. I. Price, E. F. Redknap, F. E. Ruddick, R. Smith, J. R. Taylor, J. R. Tomlinson and Miss V. M. Whitehead.

The Honorary Editor particularly wishes to thank Mr R. A. Brett and Dr V. T. Crowl (Honorary Publications Officer of London Section), who have organised the reporting, collated the reports and comments received, and written the final report.

Meeting of Council

At the Meeting of Council held on 28 February, in considering the Forward Thinking document, it was agreed for a trial period to include a brief report in the Journal of the proceedings of Council. It was appreciated that most items already appear in the *Journal* in the Notes and News section, but there were other items which might be of interest to members. The following is, therefore, the report of the meeting held on 28 February.

The Council Meeting was attended by 25 members under the chairmanship of the President, Mr F. Sowerbutts, at Wax Chandlers' Hall, Gresham Street, London EC2.

Arising from the previous meeting of the Council it was reported that Dr C. H. Wisbey had accepted Council's invitation to represent the Association in 1968 on the Technical Training Board for the Printing Ink and Roller Making Industry and that Mr R. Smith, the Association's representative on the Colour Group was willing to represent the Colour Group on the International Colour Association.

The draft Report of Council for 1967 was considered and approved, together with the Agenda for the Annual General Meeting which will take place at the Royal Hotel, Bristol, on 28 June 1968. It was agreed later in the meeting that a special resolution would appear on the Agenda authorising a change in the Articles to allow the words "Junior Member" to be replaced by the designation "Student Member."

Council then considered the Reports of the Working Parties which had been set up at the November Council meeting, on Education, Training and Qualifications under the chairmanship of Dr S. H. Bell, and on the Forward Thinking document under the chairmanship of Mr I. S. Moll. Arising from the report of the latter Working Party it was agreed that the President's Advisory Committee should be recognised as a Committee of Council and that in addition to the Honorary Officers, three Section Chairmen should serve thereon, in rotation, the first Chairmen to be from the Bristol, Irish and West Riding Sections.

It was further agreed to recommend to the Sections that Membership Surveys should be undertaken, similar to that so successfully undertaken by the Manchester Section.

Authority was given to the Director & Secretary to compile an Appointments Register as soon as possible.

Other matters were considered under this Document, but these have been referred to various Committees of Council for further consideration.

Reports were received from the Hon. Officers concerning current Association activities. Arising from these, the venue for the 1971 and 1973 Conferences were considered and it was agreed that the Conference in 1971 would take place in Dublin from 27 April to 1 May and that the venue for 1973 would probably be in the South of England, with the suggestion that in 1975 the venue would either be in Scotland or the North of England.

A full report was given on the final arrangements for the 1968 Exhibition and of the problems arising from the likely closure of Alexandra Palace in 1970 and the plans which were being made to deal with this situation.

The Provisional Income and Expenditure Account and Balance Sheet for the year ended 31 December 1967 were accepted, together with the Estimates for 1968 and the Cost Accounts.

Council resolved that members whose subscription had not been received by 31 March, in accordance with Article 14 of the Memorandum and Articles, would not be sent the Journal until payment of subscriptions due.

It was reported that the reprinting of Part I and Part II of the Paint Technology Manuals was in hand and that the History of the Association was in final course of preparation for despatch to members early in May.

The Society of Dyers and Colourists had sought assistance in relation to the solvent dyeing and pigments sections of the Third Edition of the Colour Index. Mr H. G. Cook and Dr F. M. Smith were appointed to serve in this capacity.

It was reported that it had not been found possible to award the Jordan Award on this occasion (see Notes and News, April).

Mr J. E. Pooley was nominated to serve as the Association's representative on the BSI Committee to prepare a British Standard for Water-thinned Priming Paints.

Newcastle Section

Ladies' Night

The Newcastle Section held its annual Ladies' Night on Friday 23 February at the Five Bridges Hotel, Gateshead, the scene of last year's successful event.

On this occasion the event was no less successful, attracting a record attendance of 137 members, ladies and guests.

Guests of Honour were the President, Mr F. Sowerbutts, and the Director & Secretary, Mr R. H. Hamblin. Other guests of the Section were: Mr and Mrs L. W. Wynn—Hull Section; Mr and Mrs C. H. Morris—Midlands Section; Mr and Mrs A. K. Fowler—Vice-President, Newcastle and Gateshead Branch of National Federation of Master Painters and Decorators.

In his toast to the Newcastle Section, Mr Sowerbutts spoke of the Section's long-standing interest in education which, among other things, had resulted in a very active Junior Section. The Chairman, Mr D. M. James, referred to the responsibilities which the President and the Director & Secretary bore, particularly during the current period when our Association was reviewing its position and considering changes which could greatly affect its whole structure. The Chairman welcomed this "Forward Thinking," instituted by Dr Bell, and assured Mr Sowerbutts and Mr Hamblin of the Newcastle Section's support in implementing the results of these discussions.

The photograph shows (left to right) the President (Mr F. Sowerbutts), Mr L. W. Wynn (Chairman, Hull Section), Mrs Sowerbutts, Mr D. M. James (Chairman, Newcastle Section), Mr R. H. Hamblin (Director & Secretary), Mrs James, Mrs Wynn, Mr A. K. Fowler (Vice-President, Newcastle and Gateshead Branch, National Federation of Master Painters and Decorators), Mrs Fowler, Mrs Morris, Mr C. H. Morris (Chairman, Midlands Section)

Thames Valley Section

Buffet Dance

The Thames Valley Section held their Annual Buffet Dance at the Great Fosters Hotel, Egham, on Friday 9 February. The principal guests were the President, Mr F. Sowerbutts and Mrs Sowerbutts, the Chairman of the London Section, Mr R. N. Wheeler and Mrs Wheeler, the Birmingham Section Chairman, Mr C. H. Morris and Mrs Morris, and the Director and Secretary of the Association, Mr R. H. Hamblin.

In the absence of the Section Chairman, Mr A. G. Holt who was unfortunately indisposed, Mr W. Arnott welcomed the principal guests, members and friends and their wives amounting in all to some 170 people and he thanked them for their support. Much of the interval was taken up by an excellent cold buffet. More dancing followed with numerous spot prizes and gags by the MC.

By universal consent it was a most enjoyable occasion and all praised its delightful informality. It concluded with a few kind remarks by the President, followed by Auld Lang Syne.

News of Members

Mr N. Ashworth, an Ordinary Member attached to the Manchester Section, has been appointed Chief Chemist of Leyland Paint and Varnish Co. Ltd.

Sir Christopher Cowan, an Ordinary Member attached to the London Section, has retired as Chairman of Cowan Brothers (Stratford) Limited. Sir Christopher had held the position of Chairman since 1920, and was knighted in 1958 for his services to the county of Middlesex.

Mr J. P. Davison, an Ordinary Member attached to the Newcastle Section, has been appointed Planning Manager of British Paints Limited, Mr Davison was previously Manager of British Paints' Dunston Works.

Mr R. Wilson, an Ordinary Member attached to the Newcastle Section, has been appointed Director of Operations of British Paints Limited. Mr Wilson, who was previously Research Director, has been actively concerned with the affairs of the Newcastle Section, having held the positions of Secretary and Chairman of the Section.

American Oil Chemists' Society

Papers have been invited for the AOCS 1968 Fall Meeting, to be held at the Statler-Hilton, New York City, from 20-23 October. The theme of the meeting is "Fats and oils: Progress on all frontiers," and research and development papers in any of the areas of lipids, fats and oils are welcomed. These include processing and utilisation, chemical and physical properties, analytical methodology, biochemistry and nutrition, soaps and detergents, drying oils and paints, and fatty acids and their derivatives. Closing date for application of papers is 1 July 1968.

5th AOCS Award in Lipid Chemistry

Nominations have been invited for the 5th American Oil Chemists' Society Award in Lipid Chemistry. Closing date for nominations for the Award, which consists of a $2,500 honorarium, accompanied by an appropriate scroll, is 1 August 1968. The following are extracts from the rules:

Nominees shall have been responsible for the accomplishment of original research in lipid chemistry and must have presented the results thereof through publication of technical papers of high quality.

The award will be made without regard for national origin, race, colour, creed or sex.

Letters of nomination, together with supporting documents, must be submitted in octuplicate to R. J. VanderWal, Chairman, AOCS Award Nomination Canvassing Committee, Armour & Co., Research Division, 801 W. 22nd Street, Oak Brook, Ill. 60521, before the deadline date of 1 August 1968.

The supporting documents shall consist of professional biographical data, including a summary of the nominee's research accomplishments, a list of his publications, the degrees he holds, together with the names of granting institutions, and the positions held during his professional career. There is no requirement that either the nominator or the nominee be a member of the American Oil Chemists' Society.

British Joint Corrosion Group

The Executive Committee of the British Joint Corrosion Group, of which the Association is a co-operating body, have recently issued a report on the progress of the Group. After 2½ years of effective working the Group is said to be firmly established as a major valuable body in the field of corrosion science and technology. A better climate of co-operation between the various bodies associated with the various aspects of corrosion, and confident news for the future are expressed.

Institute of Metal Finishing

The dates of the examinations of the Institute of Metal Finishing have now been set.

The Technicians Certificate Examination will be held on the morning of Saturday 8 June, and the Advanced Technicians Certificate on Friday 14 June.

Paint Research Station appoints Director

The Council of the Paint Research Association has appointed Dr G. de Winter Anderson, BSc, PhD, ARIC, as Director of Research in succession to Dr L. Valentine. Dr Anderson, who has had much experience of research and development in industry, took up his duties at the beginning of April.

Educated at the Royal Belfast Academical Institution and Queen's University, Belfast, he joined ICI Dyestuffs Division in 1949 as a research chemist, and in 1959 following a link-up between ICI and Ilford Limited, he became Group Leader in charge of photographic chemical research at ICI and a member of the liaison management committee.

In 1964 he joined Minnesota 3M Research Limited as Director of Organic Research.

Errata

The following errors have been noted in the paper by Mr P. J. Gay in the April issue:

The author's name was incorrectly stated as Mr I. H. Day on the cover of the "Journal."

Mr Gay's address was incorrectly stated, and should be Hangers Paints Limited, The Storry Smithson Group, Bankside, Hull.

The caption to Fig. 3 should read "Incorrect practice in hand spraying."

In Fig. 4 the captions have been transposed, the example stated to be the effect of the Plate too Slow should in fact be Plate too Fast, and vice versa.

We apologise to the author for any inconvenience these errors have caused.

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

BRAUCH, ERNEST WOLFGANG, MA, MS, BA, c/o International Colloids Ltd., 42 Gray's Inn Road, London WC1. (*London*)

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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.

Thursday 9 May and Friday 10 May

50th Anniversary Celebrations—Wax Chandlers' Hall.

Thursday 23 May

West Riding Section. Luncheon lecture at Astoria Restaurant, Roundhay, Leeds.

Thursday 13 to Sunday 16 June

OCCAA. Tenth Convention to be held at Hotel Florida, Terrigal, New South Wales.

Friday 28 June

OCCA Annual General Meeting. Royal Hotel, Bristol at 7.00 p.m.

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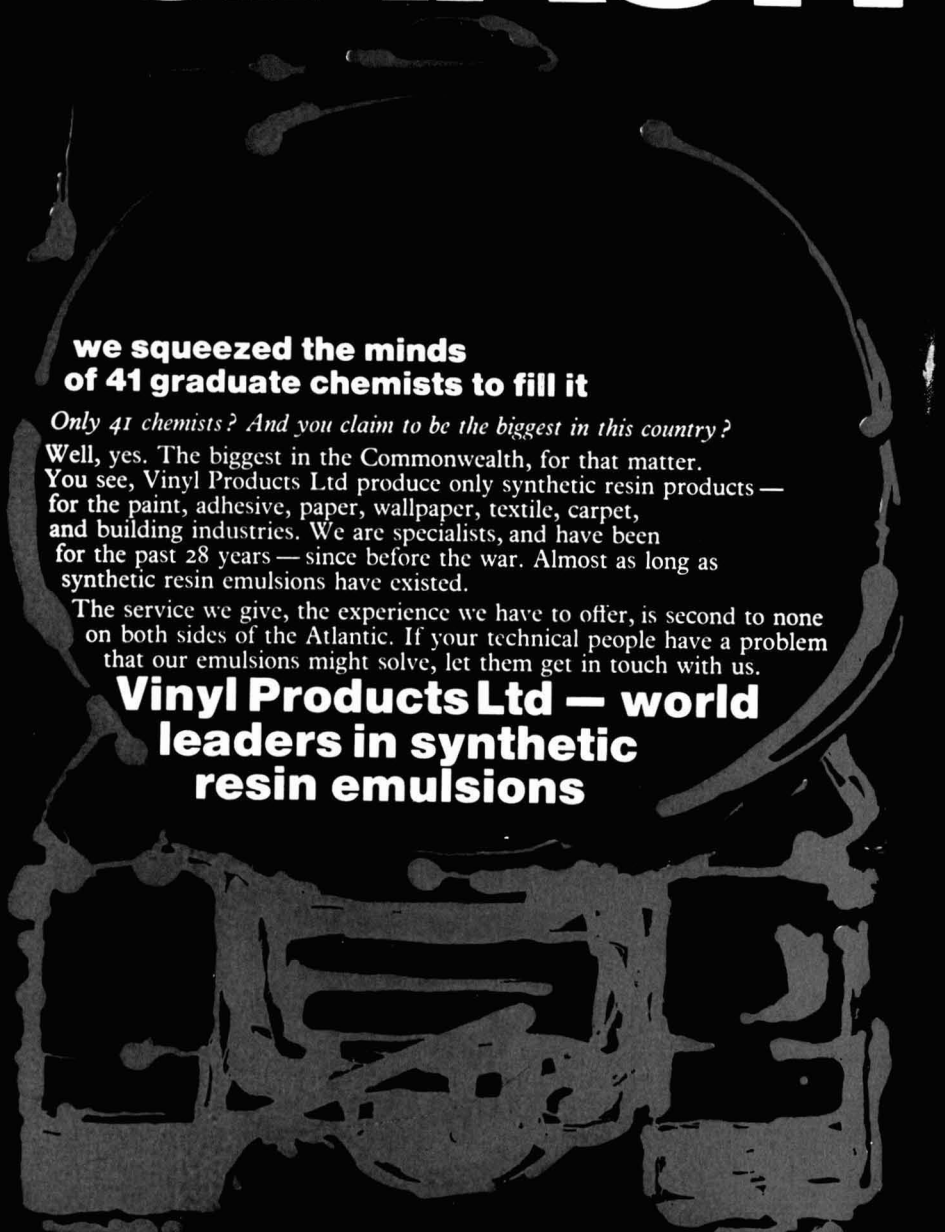

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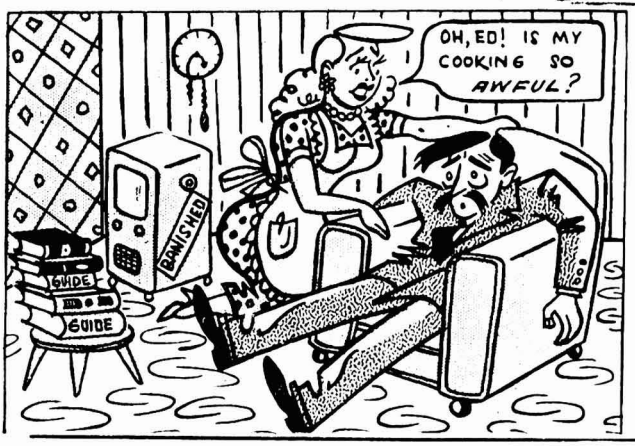

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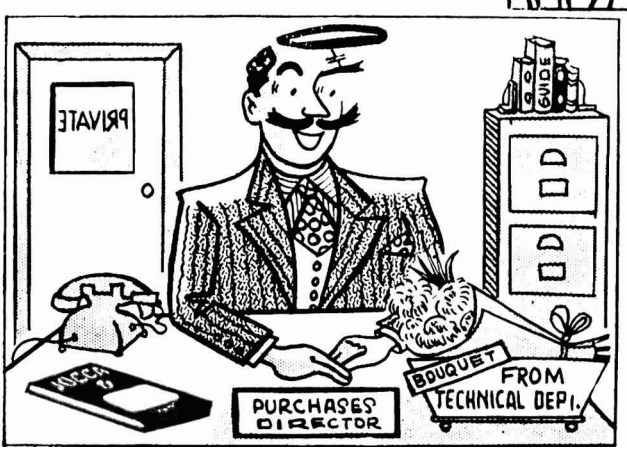

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