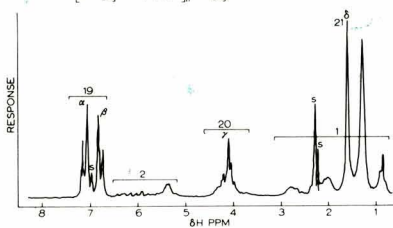
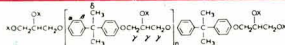




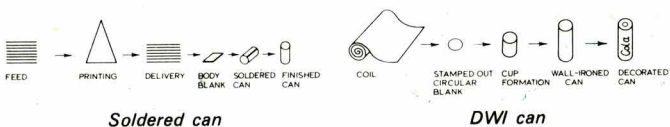
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*NMR spectrum of DCO epoxy ester*

### NMR analysis of paint media

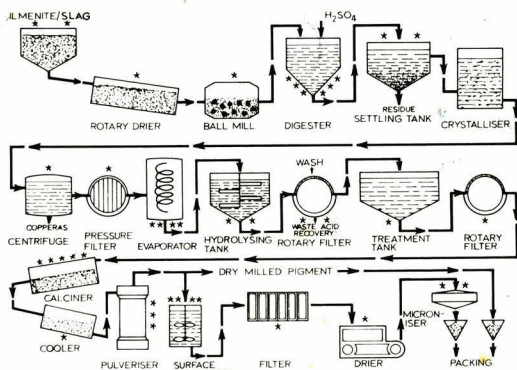
### Efficiency and change in metal decoration



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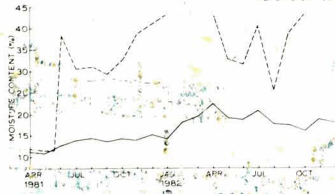
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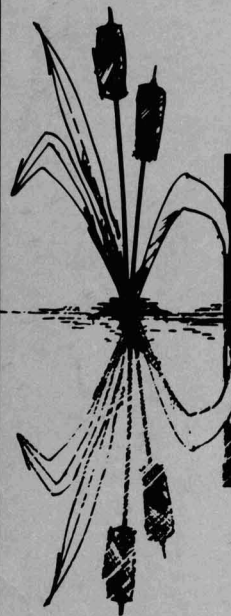
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**Contents**

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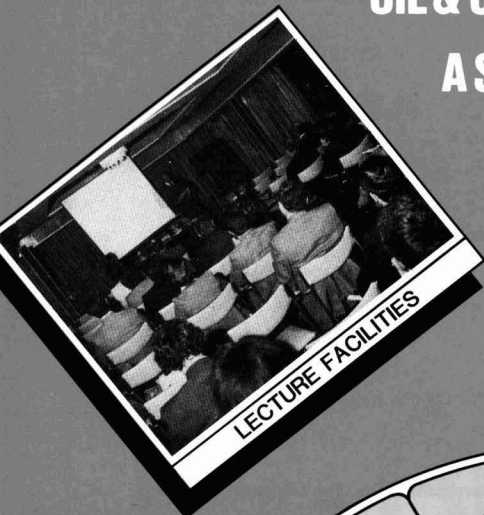
*Transactions and Communications*

<b>NMR analysis of paint media</b> .....	285
	<i>M. Marshall</i>
<b>Efficiency and change in metal decoration</b> .....	293
	<i>A. A. Gamble</i>
<b>Quality control and standardisation in the titanium pigment industry</b> .....	297
	<i>R. R. Blakey</i>
<b>Prediction of performance of exterior wood coatings</b> .....	308
	<i>E. R. Miller</i>
<b>Conference discussion</b> .....	316
<i>Next month's issue</i> .....	319
<i>Corrigendum</i> .....	319
<i>Letters</i> .....	319
<i>Reviews</i> .....	320
<i>OCCA meetings</i> .....	320
<i>News</i> .....	320
<i>Exhibition news</i> .....	325
<i>BSI news</i> .....	325
<i>OCCA news</i> .....	326

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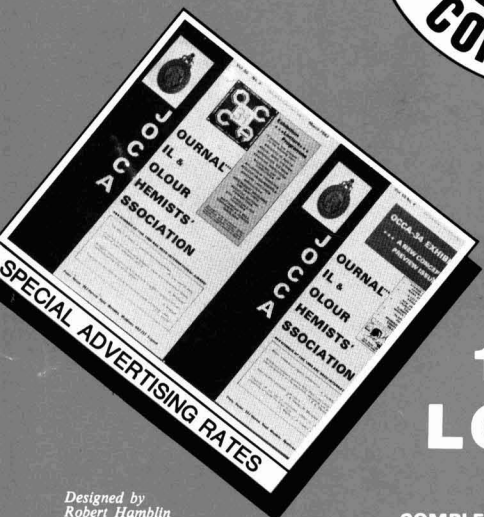
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# NMR analysis of paint media

M. Marshall

Materials Quality Assurance Directorate, Procurement Executive, Ministry of Defence, Building E135/17 Royal Arsenal East, London SE18 6TD, United Kingdom

## Summary

Examination of a range of uncured paint media has shown that valuable information can be obtained by proton NMR. Phthalate isomers, and common modifying agents such as styrene, vinyl toluene or silicones, can be identified and quantitatively determined. Drying oils can be classified into several technically significant types such as "linolenic rich" e.g. linseed oil, "simple linoleic rich" e.g. soya bean oil, "complex linoleic rich" e.g. dehydrated castor oil, "eleostearic rich" e.g. tung oil, or "non-drying"; oils can also be quantitatively determined. The successful quantitative analysis of several alkyds, modified alkyds and epoxy esters is discussed.

The proton NMR technique compares favourably with conventional procedures and is being used for routine quality assurance.

Some examples of carbon-13 NMR spectra of paint media are discussed to illustrate the future potential of the technique.

## Introduction

The composition of the binder resin employed has a crucial effect on the performance and properties of a paint system.

Analysis of binders by wet chemical methods is time consuming and sometimes difficult. Infrared spectroscopy has been widely applied for qualitative analysis but only gives limited information and has not been found well suited to routine quantitative use, not least because of problems in calibration. Gas-liquid chromatography is a valuable technique, particularly for the analysis of the fatty acid components of resins; unfortunately chemical pretreatment of the samples is necessary unless pyrolysis gas chromatography is employed. Existing methods of binder analysis are difficult, often lengthy and in some cases satisfactory methods do not exist.

Despite various studies<sup>1-4</sup> which showed considerable promise, the NMR technique has not been widely used for the analysis of paint media. In this work a range of resins employed in paints has been examined by NMR. The spectra of polymeric resins are more difficult to interpret than those of small molecules, but valuable qualitative and quantitative information can still be obtained<sup>5</sup>.

## Experimental

The proton NMR spectra were obtained with a Perkin-Elmer R32 spectrometer operating at 90 MHz. Measurements of relative peak areas were performed with the analogue integrator fitted to the spectrometer. The carbon-13 NMR spectra were obtained with a JEOL FX90Q instrument operated at 22.6 MHz. In both cases chemical shifts were measured on the delta ( $\delta$ ) scale in parts per million downfield from tetramethylsilane (TMS).

Initially samples were prepared by (a) centrifuging a diluted solution to remove pigment (in the case of a paint), (b) vacuum drying a weighed aliquot of the pigment-free solution overnight at a pressure of 0.5 mb or less. In a few

cases the presence of involatile solvents necessitated longer drying times.

Subsequently the procedure was modified to speed solvent removal by spreading the binder solutions on glass ballotini (about 125 to 250 microns in diameter) prior to vacuum drying.

Progress of drying was checked: (a) by re-weighing the samples, (b) by the disappearance of solvent peaks from the NMR spectrum. The dried samples were then dissolved in an appropriate volume of solvent to produce a 10 to 20 per cent m/v (mass/volume) solution for proton NMR, or a 30 to 50 per cent m/v solution for carbon-13 NMR.

Details of the resins examined, all of which were commercial materials, are given in tables 1 and 2. These data were mainly supplied by the manufacturers; in some cases fuller details obtained either from the literature or from analysis by other techniques are included in the tables.

## Results and discussion

### Proton NMR spectra of resins

Table 3 is a key to the proton spectra shown in figures 1 to 10.

The natural drying oils are mixtures of various fatty acid esters, the most common alcohol being glycerol. The characteristic features of the fatty acid spectra are retained in the oils, so that, for example, linseed oil, which is rich in linolenic acid, displays a triplet methyl group at 0.9 $\delta$ , whilst DCO and soya display broadened singlet methyl groups similar to that exhibited by linoleic acid. Other features characteristic of the various oils are the shape and relative intensities of the olefinic bands and the bands due to methylene groups adjacent to olefinic groups. As the molecular weight, structural complexity and sample heterogeneity increase progressively from the pure fatty acids to the oils and thence to oil modified resins, there is a corresponding gradual loss of fine detail in the NMR spectrum. However, the resins can still be reliably analysed in considerable detail, as is shown below.

### *Effect of experimental variables on the spectra of resins*

*Effect of different solvents* - A range of solvents was employed for examination of the various resins. Carbon tetrachloride, deutoacetone and deuterodimethyl sulphoxide failed to dissolve the alkyds satisfactorily and were therefore rejected, as also was trifluoroacetic acid which was found to char some samples. Deutoacetone and deuteromethylene chloride were powerful solvents, but were rejected because of their cost, volatility and large residual proton impurity peaks. Tetrachloroethylene and deuterotetrachloroethane were again excellent solvents which gave well resolved spectra. However, their only advantage was for use at elevated temperatures; deuto-

\*Paper presented at the Association's York Conference, 15-18 June 1983. An edited transcript of the discussion that followed this paper can be found on page 316.

Table 1  
Alkyds and modified alkyds<sup>7-9</sup>

Resin	Nominal composition					<sup>1</sup> H-NMR analysis				
	Phthalic anhydride (% wt)	Acids	% wt	Esterifying alcohol	Others	% wt	Phthalic anhydride (% wt)	Acids (% wt)	Others	% wt
A	32	linseed	55	glycerol		25	55			
B	23	linseed	68	pentaerythritol		20	61			
C	46	linseed	35	glycerol		39	31			
D	20	linseed	68	pentaerythritol		18	63			
E	16 terephthalate	linseed	80	pentaerythritol		13 terephthalate	71			
F	isophthalate	linseed	80	mixed		14 isophthalate	72			
G	28	low linoleic	48	pentaerythritol		34	43			
H	19	linoleic	36	glycerol	styrene	36	17	34	styrene	34
I	19	linseed	36	glycerol	vinyl toluene	36	16	39	vinyl toluene	32
J	18 isophthalate	soya	48	pentaerythritol	vinyl toluene		18 isophthalate	46	vinyl toluene	24
L	34(36)	DCO	31(53)	glycerol	phenolic resin		29	49	reference 14 in brackets. Trace of phenolic	
M		tall		pentaerythritol and trimethylolpropane	<i>p</i> - <i>t</i> -butylbenzoic acid	28	40	<i>p</i> - <i>t</i> -butylbenzoic acid	6	
O	17	tall and linoleic	62	pentaerythritol	rosin and maleic anhydride	15	60	maleic anhydride	3	
3400	29	linoleic	44	glycerol	vinyl hydrocarbon	20	21	45	styrene	15
R	16	soya	48	pentaerythritol	silicone	30	24	43	silicone	19
S	12 isophthalate	DCO and soya	48	pentaerythritol	silicone	30	10 isophthalate	42	silicone	34

Table 2  
Other resins<sup>7-9</sup>

Resin	Type	Other information	NMR results
W	epoxide ester	40% DCO acids	41% DCO acids
X	epoxide ester	48% linseed and 7% rosin = 55% acids	55% linseed acids
Y	epoxide ester	40% DCO acids	43% DCO acids
PB	phenol-formaldehyde	based on <i>p</i> - <i>t</i> -butylphenol, dibenzylether bridged	
TP	tung-phenol	50% tung oil, 50% phenyl-phenol-formaldehyde	49% tung oil, 51% phenyl-phenol-formaldehyde

tetrachloroethane was also expensive. Deuteropyridine gave large aromatic solvent effects causing changes in the spectrum compared to non-aromatic solvents; however, the preferred aromatic solvent was deuterobenzene which was cheaper and of higher isotopic purity. Overall the most useful solvent was deuteriochloroform, which was found to dissolve all the samples, gave well resolved spectra, produced only one small proton impurity peak and was the least expensive deuterated solvent.

Resins B to X were examined in both deuteriochloroform and deuterobenzene; in no case was the latter advantageous. All the spectra shown in the figures were obtained from deuteriochloroform solutions.

**Chemical modification of the samples** – Addition of acid to the sample solutions failed to produce any useful improvements in the spectra. A similarly negative result was obtained when these samples were treated with trichloroacetyl isocyanate. These results indicate that the molar concentration of free hydroxyl groups in the resins tested was very low. Any signals due to hydroxyl or acid groups are likely to be broadened by the combined effects of hydrogen bonding, steric hindrance and chemical exchange, increasing the probability of masking by signals due to the major resin components.

A rather different type of chemical modification was the addition of the lanthanide shift reagent perdeutero-tris(1,1,1,2,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium, commonly referred to as Eu(fod-d<sub>9</sub>)<sub>3</sub>, to several sample solutions. Progressive shifts of various bands occurred when increments of shift reagent were added, but these shifts were not helpful in interpretation of the spectra.

**Effect of sample temperature** – No improvements in spectra were obtained when samples in deuteriochloroform or deuterobenzene were run at 60°C or 75°C respectively, rather than the standard 35°C. Solutions in tetrachloroethylene or deuterotetrachloroethane gave better spectra at 120°C than at 35°C, but overall the results were little better than those obtained using deuteriochloroform at 35°C. All the spectra shown in figures 1 to 10 were run at 35°C.

Table 3  
Key to proton NMR spectra, figures 1 to 10

Symbol	Assignment
s	solvent
1	fatty acid alkyl
2	fatty acid olefin
3	polyol
4	<i>o</i> -phthalate
5	isophthalate
6	terephthalate
7	styrene aromatic
8	styrene alkyl
9	vinyl toluene aromatic
10	vinyl toluene alkyl
11	phenolic resin aromatic
12	<i>p</i> - <i>t</i> -butyl benzoate aromatic
13	<i>p</i> - <i>t</i> -butyl benzoate: <i>t</i> -butyl
14	maleate
17	silicone aromatic
18	silicone alkyl
19	epoxide resin aromatic
20	epoxide resin glycidyl
21	epoxide resin alkyl
22	phenolic resin:dibenzyl ether bridge
23	phenolic resin:methylene bridge
24	<i>t</i> -butylphenol: <i>t</i> -butyl

## Qualitative analysis of resins

**Alkyd resins** – Figures 1 to 7 show the proton spectra of a series of alkyds and modified alkyds. The spectra of the samples show some common features.

Thus, drying oil fatty acids give rise to a series of bands due to olefinic groups, methylene groups next to or between carbon-carbon double bonds, backbone methylene groups, and terminal methyl groups. The alkyds also display bands in the range 3.2δ to 5.4δ due to esterifying alcohols. Bands in the range 3.2δ to 3.9δ arise from the presence of both ether groups, e.g. in dipentaerythritol, and unreacted polyol. The methylene groups in glycerol and pentaerythritol esters absorb in the range 3.9δ to 4.6δ whilst the methine protons in glyceryl esters absorb at 5.0δ to 5.4δ. This latter band overlaps slightly with the fatty acid olefinic bands, but this is ignored in the calculations below since the resulting error is small. Although these alcohol bands differ between samples, their complex origin prevents easy qualitative identification of the alcohols; however, this does not prevent their quantitative determination. The discussion below concentrates on those features of the spectra which are distinctive and assist in identification. Common features such as backbone methylene bands or alcohol bands are not generally discussed.

Resin E, Figure 1, shows the characteristic triplet at 0.9δ due to the methyl group of linolenic acid, the major

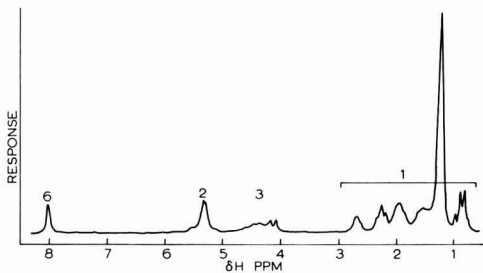


Figure 1. Resin E: linseed/terephthalic/pentaerythritol alkyd

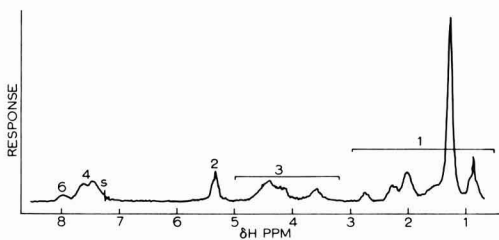


Figure 2. Resin G: linoleic alkyd

constituent of linseed fatty acids. Resins H, Figure 3, and M, Figure 6, exhibit aromatic bands at 7.2δ to 7.8δ assigned to *o*-phthalate, whilst resin E has a broad singlet at 7.9δ to 8.1δ due to terephthalate. Resin G, Figure 2, shows bands at 7.2δ to 7.8δ assigned to *o*-phthalate, together with a small band at 8.0δ probably due to the presence of some terephthalate. Finally the fatty acid in resin G shows a particularly large band at 2.0δ together with a small band at 2.8δ. This pattern is typical of "simple linoleic rich" acids such as those from soya bean oil.

A series of modified alkyds' spectra are shown in figures 3 to 7. Modifications which involve reaction with

the olefinic double bonds of the fatty acids reduce or eliminate the characteristic spectral features due to the particular fatty acids.

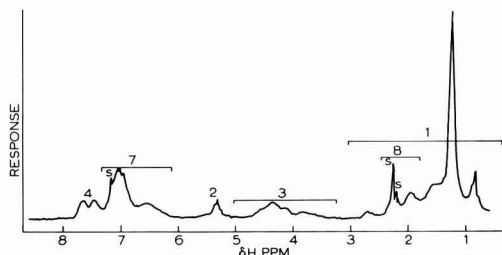


Figure 3. Resin H: styrene modified alkyd

Resin H, shown in Figure 3, is a styrene modified alkyd. Bands at 7.3δ to 7.8δ due to *o*-phthalate, and at 6.2δ to 7.3δ due to polystyrene, are readily identified, as are the bands due to esterifying alcohol at 4.0δ to 5.2δ. The signals between 3.2δ and 4.0δ suggest the presence of some unreacted or etherified polyol. The alkyd protons of the polystyrene overlap with the alkyd protons of the fatty acids and allowance for this must be made when calculating the quantitative composition.

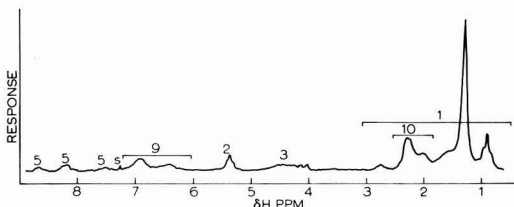


Figure 4. Resin J: vinyl toluene modified alkyd

Figure 4 shows a vinyl toluene modified alkyd, resin J. The three bands in the ratio 1:2:1 at 7.5δ, 8.2δ and 8.6δ are due to isophthalate. The polyvinyltoluene gives rise to broad aromatic bands at 6.9δ and 6.4δ and a methyl band at 2.3δ which is sufficiently intense to be distinguished above the fatty acid methylene signal which it overlaps. The other alkyd bands of the polyvinyltoluene are obscured by the fatty acid signal.

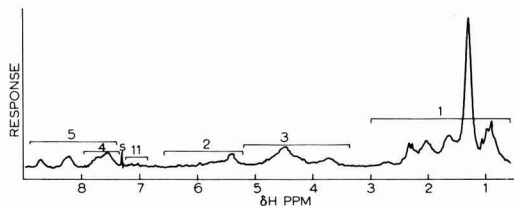


Figure 5. Resin L: phenolic modified alkyd

Resin L, Figure 5, is described as a short oil alkyd modified with DCO and phenolic resin, and esterified with glycerol. Examination of the aromatic region of the NMR spectrum indicates the presence of both *ortho*- and *isophthalate*, as well as a very weak band around 7δ possibly due to a small amount of phenolic resin. The presence of a "complex linoleic rich" fatty acid such as DCO is suggested by the series of small peaks between 6.5δ and 5.5δ. An unusual feature of this spectrum is the residual fine structure apparent in the methyl band at 0.9δ; this suggests the presence of some linolenic acid.

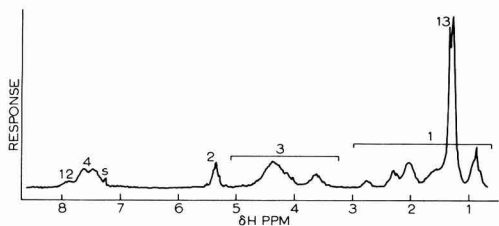


Figure 6. Resin M: modified alkyd

Figure 6 shows the spectrum of resin M, a tall oil alkyd modified with *p*-*t*-butyl benzoic acid and esterified with a mixture of pentaerythritol and trimethylolpropane. The fatty acid bands indicate a "simple linoleic rich" type oil such as soya or tall oil. The very sharp peak at 1.3δ on the downfield side of the main alkyl peak may be assigned to the *t*-butyl group of the *p*-*t*-butyl benzoate, whilst the aromatic part of this modifying agent produces one band at 7.8δ and another which is obscured by the phthalate.

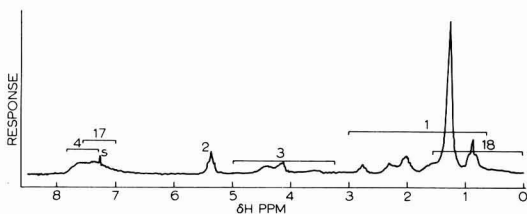


Figure 7. Resin R: silicone alkyd

A silicone alkyd, resin R, is shown in Figure 7. The fatty acid is evidently of the "simple linoleic rich" type and in fact is declared to be soya. The presence of *o*-phthalate may be deduced from the band at 7.8δ to 7.2δ, which overlaps with the aromatic silicone band at 7.2δ. Alkyl silicone groups are responsible for the broad weak band at 0.8δ to 0.0δ, which overlaps with the fatty acid alkyl bands. The use of deuterobenzene rather than deuteriochloroform as solvent did change the aromatic region of this sample's spectrum, but did not resolve the overlap.

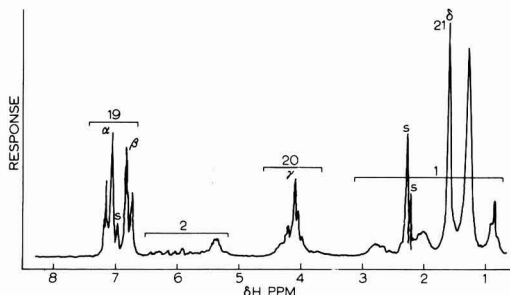
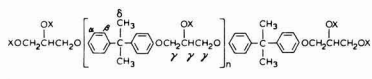


Figure 8. Resin W: DCO epoxy ester

**Epoxy resins** – The assigned spectrum of W, a DCO epoxy ester, is shown in Figure 8. As previously, the DCO fatty acid can be readily identified, as can the presence of bisphenol A epoxy.

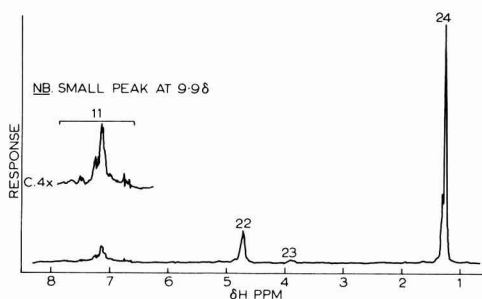


Figure 9. Resin PB: phenol-formaldehyde resin

**Phenolic resins** – Figure 9 shows the spectrum of a *p*-*t*-butyl phenol-formaldehyde resin, PB. This is a dibenzyl ether bridged resin, as indicated by the band at 4.7δ. A small band at 3.9δ suggests the presence of some methylene bridges, and there is a very small band at 5.2δ possibly due to free hydroxyl. This resin also exhibits a weak signal at 9.9δ, which indicates the presence of some aldehyde groups. The wide variety of chemical environments present in this sample is shown by the complexity of the aromatic bands and the splitting of the *t*-butyl signal at 1.2δ.

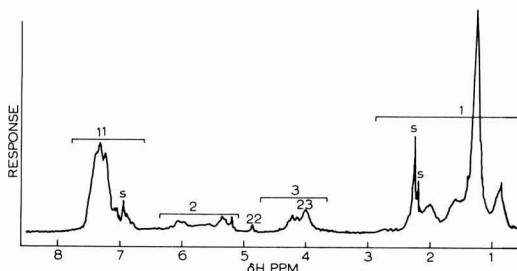


Figure 10. Resin TP: tung-phenolic resin

Resin TP, Figure 10, is produced from a phenylphenol-formaldehyde resin and tung oil. The aromatic bands due to the phenylphenol are seen at 7.5δ to 6.7δ, whilst dibenzyl ether bridges or methylol groups give rise to the small band at 4.8δ. Methylene bridges in the phenolic resin are responsible for the band at 3.9δ superimposed on the glycerol band from the oil. The characteristic olefinic bands from tung oil are clearly visible in the range 5.0δ to 6.0δ, with a small extra peak at 5.2δ probably due to phenolic hydroxyls. Another notable feature of the oil spectrum is the virtual absence of any band at 2.8δ arising from methylene groups between two olefinic groups; these are of course absent in eleostearic acid, the major component of the tung oil fatty acids.

#### Scheme for proton NMR analysis of resins

It is clear from the results above that proton NMR offers valuable detailed information on the qualitative composition of paint media.

However, the detailed nature of the information obtainable, and the wide variety of resins which may be encountered, make some rationalisation of the analytical process highly desirable. One possible approach is the construction of a flow chart for proton NMR analysis of paint resins; a similar method has been used, for example, in the infrared analysis of resins<sup>15</sup>.



Table 4  
Flow chart for proton NMR analysis of paint media

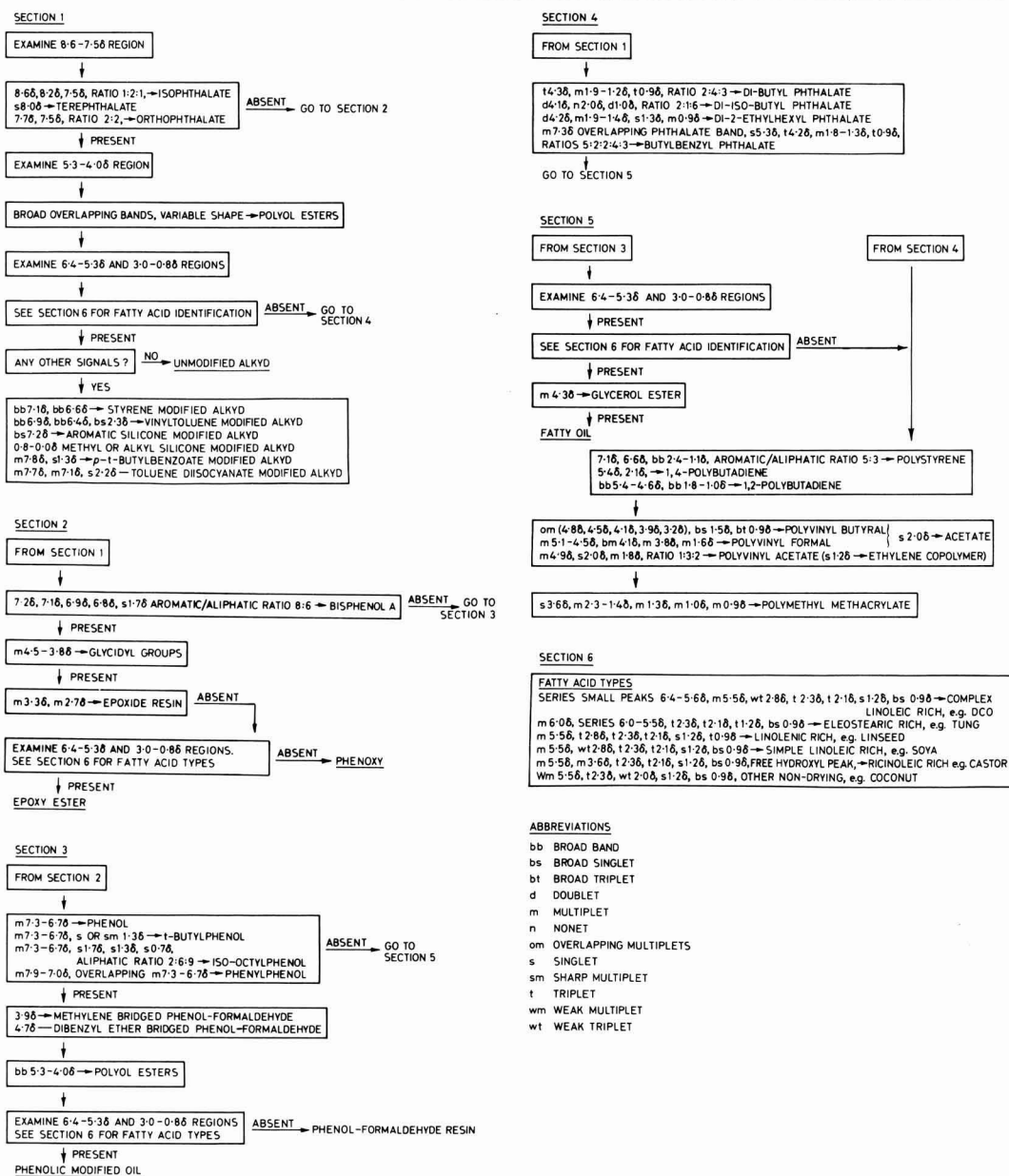


Table 4 represents an attempt to construct such a flow chart. As usual the analyst starts at section 1 of the chart, by examining the low field region of the sample's spectrum, and is then guided through the various stages to a result. Although no chart of this type can be fully comprehensive, the proposed system should enable successful analysis of most common paint resins.

#### Quantitative analysis of resins by proton NMR

Since the area of each of the individual NMR absorption bands is directly proportional to the number of protons causing that band, measurement of the relative areas of bands enables calculation of the sample composition. Examples of the procedure are given below, whilst

Table 5  
Assumed average composition factors for proton NMR analysis<sup>6,10,11</sup>

Compound	Number of protons	Molecular weight	Proton equivalent weight
DCO acids	31.5	281.0	
Linseed acids	30.9	280.3	
Soya bean acids	31.9	281.4	
Tall oil acids	31.9	279.2	
Tung acids	29.9	279.4	
Coconut acids	23.6	205.5	
Other fatty acids	32.0	280.0	
Phthalic anhydride	4	148.1	37.0
Phthalic acids	4	166.1	41.5
Glycerol	5	92.1	18.4
Pentaerythritol	8	136.1	17.0
Trimethylolpropane	6	134.2	22.4
Butylbenzoic acid	4	178.2	44.6
Styrene	5 aromatic	104.2	20.8
Styrene	3 alkyl	104.2	34.7
Vinyl toluene	4 aromatic	118.2	29.6
Vinyl toluene	6 alkyl	118.2	19.7
Hydroxy functional	} aromatic		37.6
		alkyl	52.1
Silicone additive	} hydroxyl		266.5

tables 1 and 2 give comparisons between the NMR and expected results. Table 5 shows the values assumed for the various factors used in the calculations.

(a) Resin H

Chemical shift	Assignment	Integral
8.0–7.3δ	<i>ortho</i> -phthalate (4H)	16.0
7.3–6.0δ	styrene aromatics (5H)	55.0
6.0–5.0δ	olefinic	12.0
5.0–4.2δ	glycerol (5H)	26.6
2.9–0.6δ	alkyls	144.8

First calculate the integral due to fatty acid, allowing for overlap by the alkyl protons of the styrene.

Integral due to alkyl protons of styrene

$$= 55.0 \times 3/5 = 33.0$$

Integral due to fatty acid

$$= 144.8 + 12.0 - 33.0 = 123.8$$

Mole ratio of phthalic anhydride/styrene/glycerol/fatty acids

$$= 16.0/4 : 55.0/5 : 26.6/5 : 123.8/32$$

$$\text{i.e. } 1 : 2.75 : 1.33 : 0.967$$

The weight ratios of the ingredients are then given by the mole ratios multiplied by the molecular weights.

Therefore weight ratios of ingredients

$$= 1 \times 148.1 : 2.75 \times 104.1 : 1.33 \times 92.1 : 0.967 \times 280$$

giving a composition of 17.9 per cent phthalic anhydride, 34.6 per cent styrene, 14.8 per cent glycerol, and 32.8 per

cent fatty acids. This compares with accepted values of 19 per cent phthalic anhydride, 36 per cent styrene, and 36 per cent fatty acids.

It is important to note that these results are calculated on an ingredient basis, and that no allowance has been made for the effect of loss of water during resin esterification. Consequently the NMR analysis would be expected to yield higher figures for polyol content and lower figures for other ingredients than a similar conventional analysis.

(b) Resin W

Chemical shift	Assignment	Integral
7.5–6.5δ	bisphenol A aromatic (8H)	45.3
6.5–5.0δ	fatty acid olefin	16.8
5.0–3.4δ	glycerol (5H)	33.7
3.0–0.6δ	alkyl groups	147.8

First calculate the integral due to fatty acid, allowing for overlap by the methyl groups of bisphenol A.

Integral due to bisphenol A methyls

$$= 45.3 \times 6/8 = 34.0$$

Integral due to DCO acids

$$= 147.8 + 16.8 - 34.0 = 130.6$$

Mole ratio of bisphenol A/glycidyl/DCO acids

$$= 45.3/8 : 33.7/5 : 130.6/31.5 = 1 : 1.1903 : 0.7322$$

Assume the structure of the epoxy ester to be as shown in Figure 8. The next stage is to calculate the equivalent weight of the original epoxide resin used.

Mole ratio (E) glycidyl/bisphenol A

$$= (n + 2)/(n + 1) \text{ i.e. } n = (2 - E)/(E - 1)$$

Since  $E = 1.1903$ , then  $n = 4.255$ ; hence the number average molecular weight is given by  $M_N = 340 + 4.255 \times 284 = 1548$ , where 340 is the formula weight of the epoxide functional end groups, and 284 is the formula weight of the repeat units in the original epoxide resin.

The functionality of the epoxide resin =  $n + 4 = 8.255$

Therefore, equivalent weight =  $1548/8.255 = 188$

The oil length of the epoxy ester, defined as the mole ratio of epoxide resin functional groups to acid, can now be calculated. The number of epoxide resin reactive sites (i.e. hydroxyls and epoxides) =  $[(n + 4)/(n + 1)] \times$  number of bisphenol A groups in the resin.

i.e. mole ratio of reactive sites in resin to acid

$$= (n + 4)/(n + 1) \times 1 : 0.7322$$

$$= (8.255/5.255) \times 1 : 0.7322$$

$$= 1 : 0.4661$$

which gives an oil length of 47 per cent.

The composition can then be calculated:

Ingredient	Equivalent weight	Weight used	Percentage weight
Epoxide resin	188	188	59
DCO acids	281	132	41

This compares with an accepted value of 40 per cent DCO acids.

Determination of the molecular weight of the original epoxide resin, as above, requires some care in sample preparation and spectrometer adjustment. In many cases it is sufficiently accurate to assume a typical value for the epoxide resin equivalent weight, thereby simplifying the procedure.

A more difficult problem arose in the analysis of the silicone alkyds, since in this case the structure of the modifying agent was not known. However, a sample of the silicone additive was obtained from the resin manufacturer and its proton equivalent weight (i.e. molecular weight divided by number of protons) determined. This factor was then used in the analysis.

Replicate analyses of resin H were undertaken to assess the reproducibility of the proton NMR technique. Table 6 gives the results.

The agreement between the nominal figures and the NMR results in tables 1 and 2 is generally satisfactory, as is the reproducibility shown in Table 6. Generally it would be expected that the NMR results for fatty acid and phthalate content of the alkyds would be slightly lower than the accepted values since the NMR figures make no allowance for loss of water during esterification.

Some modifying agents present difficulties in quantitation. Thus maleic anhydride may react with the resin in at least three ways: (a) esterification, giving rise to a maleate band at about  $\tau_6$ ; (b) crosslinking reactions via the olefinic bonds in the drying oil; (c) Diels-Alder addition to dienes in the oil. Reactions (b) and (c) would result in alkyl signals causing an erroneously high result for fatty acid content. Silicone modification of alkyds also causes some difficulty, both because of the unknown structure of the

Table 6  
Replicate analysis of resin H

Phthalic anhydride (% w/w)	Styrene (% w/w)	Glycerol (% w/w)	Fatty acids (% w/w)
17.9	34.6	14.8	32.8
17.9	33.5	14.8	33.8
16.9	35.6	14.0	33.5
17.1	34.3	14.9	33.7
17.1	34.2	14.9	33.9
17.0	34.1	14.9	34.1
18.2	33.3	14.8	33.7
Mean			
17.4	34.2	14.7	33.6
% standard deviation			
3.1	2.2	2.2	1.2

Table 7  
Key to carbon-13 NMR spectra, figures 11 to 13

Symbol	Assignment
A	C <sub>1</sub> (S, O, LO, LE)
B	C <sub>16</sub> (LE)
C	C <sub>9,10</sub> (O), C <sub>9,13</sub> (LO), C <sub>9</sub> (LE)
D	C <sub>10,12</sub> (LO), C <sub>10,12,13</sub> (LE)
E	C <sub>15</sub> (LE)
G	C <sub>2</sub> (S, O, LO, LE)
H	C <sub>16</sub> (S, O)
I	C <sub>16</sub> (LO)
J	C <sub>4-15</sub> (S), C <sub>4-7</sub> (O, LO, LE), C <sub>12-15</sub> (O), C <sub>15</sub> (LO)
K	C <sub>8,11</sub> (O), C <sub>8,13</sub> (LO), C <sub>8</sub> (LE)
L	C <sub>11</sub> (LO, LE), C <sub>14</sub> (LE)
M	C <sub>3</sub> (S, O, LO, LE)
N	C <sub>17</sub> (S, O, LO)
O	C <sub>17</sub> (LE)
P	C <sub>18</sub> (S, O, LO, LE)
a	carbonyl (PA, IPA, TPA)
b	C <sub>1,4</sub> (TPA)
d	C <sub>4,6</sub> (IPA)
e	C <sub>1,6</sub> (PA)
f	C <sub>1,2,3</sub> (IPA), C <sub>3,6</sub> (PA)
g	C <sub>2,3,5,6</sub> (TPA)
h	C <sub>4,5</sub> (PA), C <sub>5</sub> (IPA)
$\alpha$	C <sub>3</sub> glycerol
$\beta$	C <sub>1,3</sub> glycerol
$\delta$	methylol of pentaerythritol
$\epsilon$	quaternary carbon of pentaerythritol

Abbreviations: S = stearic acid, O = oleic acid, LO = linoleic acid, LE = linolenic acid, PA = *o*-phthalate, IPA = isophthalate, TPA = terephthalate

modifying agent, and, as seen in the case of resin R, overlap with the phthalate bands.

### Carbon-13 NMR

The carbon-13 NMR spectrum of linseed oil has been analysed in detail<sup>12,13</sup> as have some other oils. Similar to proton NMR, many of the characteristic features of the oils are retained in the alkyds and differentiation of oils is relatively easy. Table 7 gives a key to the subsequent carbon-13 NMR spectra.

The carbon-13 spectra of resins E and G were obtained from deuteriochloroform solutions at 50°C, using gated decoupling to eliminate the nuclear Overhauser effect. The relaxation agent chromium acetylacetonate was added to resin R, whose spectrum was obtained at 40°C. Accumulation times of about seven hours were necessary to obtain satisfactory spectra.

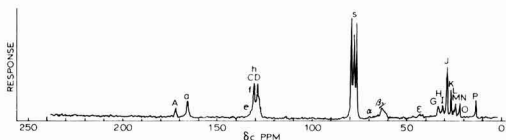


Figure 11. Resin G: linoleic alkyd

Figure 11 shows resin G, a linoleic rich *o*-phthalate alkyd esterified with mixed polyols. Clearly separated signals are obtained for the aliphatic and aromatic carbonyls at about 174 $\delta$  and 167 $\delta$  respectively. The aromatic ring carbons of the phthalate overlap with, and are obscured by, the olefinic carbons of the fatty acids. In fact the region around 130 $\delta$  is dominated by the olefinic doublet from the linoleic acid. Three groups of signals may be assigned to the polyol: a very weak multiplet about 70 $\delta$ , a multiplet around 63 $\delta$  and another weak multiplet about 43 $\delta$ . Examination of model compounds such as tristearin, trilinolein and pentaerythritol tetrastearate showed that in these aliphatic esters the primary and secondary carbons of glycerol gave signals at 62 $\delta$  and 69 $\delta$  respectively, whilst the primary and quaternary carbons of pentaerythritol gave signals at 63 $\delta$  and 43 $\delta$ . It is therefore probable that resin G contains both glycerol and pentaerythritol.

Examination of the aliphatic signals between 35 $\delta$  and 0 $\delta$  confirms the description of G as a linoleic rich alkyd.

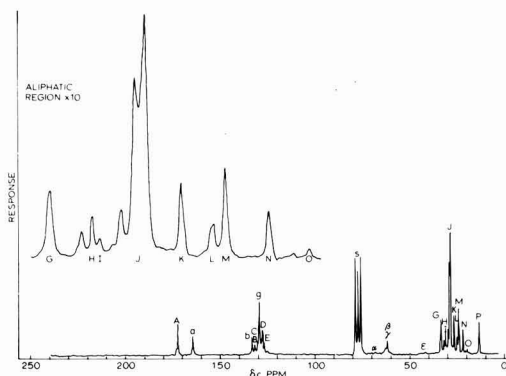


Figure 12. Resin E: linseed/terephthalic/pentaerythritol alkyd

Resin E, Figure 12, again shows the presence of both glycerol and pentaerythritol. This is a spectrum of a small sample which had been stored for several years in a partly filled container. The expanded version of the aliphatic spectral region illustrates both the great detail of the information available in the carbon-13 spectrum, with several well separated peaks characteristic of individual fatty acids, and also the fact that oxidative attack has, as expected, occurred preferentially on the linolenic component of the alkyd. Loss of linolenic acid is indicated by the diminished size of peak "O" at 20 $\delta$  compared to the same peak in fresh linseed alkyls.

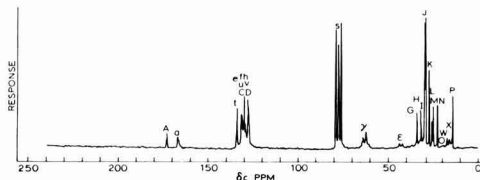


Figure 13. Resin R: silicone alkyd

A silicone modified soya alkyd, R, is shown in Figure 13. Again it is possible to recognise the presence of linoleic rich fatty acids and pentaerythritol. Two small peaks at 16 $\delta$  and 17 $\delta$  are due to the alkyd silicone groups; the aromatic signals of the silicone and phthalate occur about 130 $\delta$ , overlapping with the fatty acid olefins.

Quantitative analysis is possible by carbon-13 NMR, although quantitative measurements may require seven or more hours even when relaxation agents such as chromium acetylacetonate are used. Thus for resin E the following results were obtained:

Area of carbonyl "A"	= 6.8
Area of carbonyl "a"	= 5.0
Area of polyol CH <sub>2</sub> "β, δ"	= 8.2

Taking the polyol as mainly pentaerythritol, the mole ratio of linseed acid/terephthalic acid/pentaerythritol equals

$$6.8/1 : 5.0/2 : 8.2/4 = 1 : 0.3676 : 0.3015$$

Therefore, the weight ratio of the ingredients equals

$$1 \times 280.3 : 0.3676 \times 166.1 : 0.3015 \times 136.1 = 280.3 : 61.1 : 41.0$$

giving 73 per cent linseed and 16 per cent terephthalate, compared to accepted values of 80 per cent and 16 per cent.

A similar analysis of resin G gave 52 per cent fatty acid and 26 per cent phthalic anhydride, compared to accepted values of 48 per cent and 28 per cent.

## Conclusions

Valuable qualitative and quantitative information about the composition of uncured alkyls, modified alkyls, epoxy esters and other paint media can be obtained by NMR.

Particular advantages of proton NMR over other techniques are its speed, simplicity and ease of calibration.

Examination of the proton NMR spectrum of oil modified media allows classification of the common drying oils into technically significant groups:

- (i) Linolenic rich, e.g. linseed oil
- (ii) Eleostearic rich, e.g. tung oil
- (iii) Complex linoleic rich, e.g. DCO
- (iv) Simple linoleic rich, e.g. soya or tall oil
- (v) Ricinoleic rich, e.g. castor oil
- (vi) Non-drying oils

Quantitative determination of drying oil fatty acids is also possible.

The phthalate isomers incorporated in alkyls can be



both identified and quantified, and isomer ratios in phthalate mixtures can be determined.

Common modifying agents such as styrene, vinyl toluene and silicones can be identified and determined in alkyds and other resins.

Identification of polyols in alkyds cannot be accomplished by proton NMR, however determination of known polyols is possible.

Carbon-13 NMR, although a relatively slow technique, has the merit of providing more detailed information about the structure of organic materials than can be gained from any other current analytical technique.

Polyol identification and determination is possible by carbon-13 NMR.

It may be possible to develop the carbon-13 NMR technique further to provide detailed fatty acid profiles of resins comparable to those obtained by chromatographic methods.

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Mr J. E. Davies and Dr G. L. Marshall assisted with some of the experimental work. Resin samples were supplied by several manufacturers.

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## Efficiency and change in metal decoration

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### 1. Introduction

The last decade has seen significant changes in metal decorating techniques, particularly in metal container design and associated printing methods. Printing is no longer restricted to a flat sheet, as modern equipment can print in a circular mode in a variety of ways.

Since the first flat-topped beer can appeared in 1954, beer and beverage can design and decoration have changed significantly. Printing ink technology has had to keep pace with these changes and products are being continually upgraded as requirements demand.

Whilst flat sheet printing is still the basis for a high percentage of decorated work, changes have taken place in image design together with the technology of container formation. Distort printing for example is a new area that utilises traditional printing equipment together with computer design and modern coating materials. Computers are now regularly used to calculate image forms when printing on a flat surface, a surface which subsequently is distorted into the final container shape.

This paper attempts to review changes that have taken place and are still taking place within the metal decorating market. It tries to show the interrelationship of container design and printing ink technology and uses this to speculate as to some potential future developments.

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### 2. The metal decorating market in focus

Printed metal articles have for many years fallen into classifications recognised throughout the metal finishing industry. For convenience it is easier to review the changes in technology within these groups, and for ease of discussion the author has added further groups and sub-groups as necessary.

Hence, for the purpose of this review the printed metal market has been divided into the following sections:

#### 2.1 Open top containers

#### 2.2 General line work

##### 2.2.1 Drums

#### 2.3 Crowns and closures

#### 2.4 Miscellaneous; extrusions, dials, implements, etc.

#### 2.1 Open top containers

The open top market is exclusively concerned with beer and beverage containers. The derivation of open top has its roots in the fact that all the containers were transported "open" to the appropriate filling lines, where they were filled and sealed.

\*Paper presented at the Association's York Conference, 15-18 June 1983. An edited transcript of the discussion that followed this paper can be found on page 316.

## 2.2 General line market

The general line market covers virtually all other printed metal articles. Containers such as oil cans, biscuit tins, boot polish containers, paint cans and aerosol containers all come under the heading of general line work. Other more specific articles of general line work are considered separately:

### 2.2.1 Drums

The drum container market has been separated for convenience as it is not only a substantial part of the total general line market but in many cases drum printing is physically separate from other product lines.

### 2.3 Crowns and closures

This market area covers all printed container closures – from bottle crowns to “spirit bottle” closures and “vacuum sealing” jar caps.

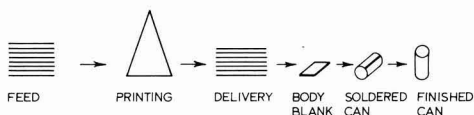
### 2.4 Miscellaneous

For convenience all other printed metal objects are considered under this heading. The range is very wide and covers small areas in terms of market share such as metal dial printing to larger market areas such as extrusion printing for toothpaste tubes, drug containers, battery cases, penholders, etc.

## 3. Open top printing

Traditionally, open top containers were printed in flat sheet form, largely by lithographic means but occasionally by the dry offset process. Multiple passes through the oven were required as no inter-colour superimposition was possible where wet ink films were concerned. Consequently, printing lines were rarely seen containing more than a two-colour press. Body blanks were then punched out from the composite sheet and sealed into a tube, historically via a soldered side strip. A base and – after filling – a top then completed the container.

This can be represented diagrammatically as follows:



Developments in open top can technology and decoration are described below.

### 3.1 Ink technology – flat sheet printing (soldered cans)

Such a process demanded many different properties from the ink. The important requirements were:

3.1.1 Good lithographic properties.

3.1.2 Hard drying in the prescribed stoving time scale.

3.1.3 Hard enough to resist scratching but must accept varnishing.

3.1.4 Good adhesion to the basecoat and adequate flexibility to withstand tooling.

3.1.5 Colours should not be affected by heat from soldering (particularly critical for tints).

3.1.6 Dried film should withstand any processing necessary before or after can filling. Pasteurisation is perhaps the most common.

### 3.2 UV Technology

In order to facilitate faster turnround of work and/or in-line dry trapping of different colours, inks were introduced that polymerised under ultraviolet light. The advantages of UV curing technology both practically and theoretically have received considerable publicity elsewhere<sup>1</sup>. The main practical advantages found with UV curing technology are:

3.2.1 Interdeck curing (i.e. UV curing facilities stationed between printing units in the line).

The predominant advantage to the printer with interdeck UV curing is the increased flexibility of his operation. He can now trap one colour over the “cured” film of another colour, thus reducing the number of passes through the printing line on multiple colour operations.

3.2.2 Set-stack curing (i.e. UV curing facilities stationed at the end of the line in lieu of a conventional thermal oven).

The predominant advantage with set-stack curing is the utilisation of space. A printing line can be fitted into a relatively small area thus increasing capacity at relatively low expense.

Early UV beer and beverage cans were soldered giving the same problems as conventionally decorated containers. The soldered side-seal was an obvious area of attention to improve the appeal and leakage problems inherent in the design.

### 3.3 Problems with the soldered can

The soldered can has now virtually been replaced with superior alternatives. These alternatives are discussed at length later. It is, however, important to examine the reasons why soldered cans have been superseded. The problems associated with soldered cans are summarised as follows:

3.3.1 In order to ensure that the heat from the soldering operation does not affect the printed area, an unprinted gap has to be left at the edges of the design. This discontinuous design is not appealing.

3.3.2 The wide solder band is ugly.

3.3.3 Lead in the solder gives rise to problems in recycling containers and possibly of food contamination.

3.3.4 Small pinholes in the soldered joint often occur giving rise to leakage of the contents.

### 3.4 The welded can

The development and emergence of the welded side-seam yielded many of the required improvements over the soldered side-seam. The advantages and disadvantages are summarised as follows:

## Advantages

3.4.1 Smoother seam – the side-seam is neater and smoother producing an aesthetically improved design overlap due to the reduced design discontinuity.

3.4.2 Absence of lead – the absence of lead means that recycling is easier as lead contamination no longer applies.

3.4.3 Reduced leakage of contents – this is achieved through better sealing. Leakage is still a problem, however, as discussed below.

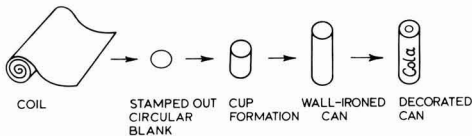
## Disadvantages

3.4.4 Small (or large) filaments of varnish, splashing onto the side-stripe area can cause welding failure and may result in leakage. Splashing is hard to eliminate when dealing with low viscosity lacquers.

Although the move to welded cans offered advantages over soldered cans, development of the two-piece can (DWI can) and the complete elimination of the side-seam heralded a much greater potential reduction in leakage.

## 3.5 The DWI container

The two-piece container (DWI can) as its name implies is produced as a complete body and base and requires only a top for completion. The body and base are formed from a single piece of metal (aluminium or tin-plated steel) and moulded/wall ironed into shape. This is shown diagrammatically below:



The printing of this type of container takes place in the round and nowadays little overvarnishing is done. The advantages and disadvantages of the DWI can are as follows:

## Advantages

3.5.1 No join hence design is aesthetically more attractive.

3.5.2 No join hence leakage is reduced.

3.5.3 No lead used hence no associated problems in recycling or of food contamination.

3.5.4 Much less metal is used hence cheaper raw material costs.

3.5.5 No overvarnishing means the saving of a unit on the press.

## Disadvantages

3.5.6 Printing in the round via dry offset (offset letterpress) is limiting from the design point of view. Quality half-tone is far more difficult to achieve from a direct printing mode.

3.5.7 Ink misting is a common occurrence.

The change to the DWI container with its associated

stoving and critical mobility changes has demanded a change in ink technology. The changes necessitated are as follows:

## DWI ink requirements

3.5.8 Oven dwell times vary depending upon the type used. Short cycle (high temperature) ovens, for example, have a residence time of around seven seconds.

Inks for DWI containers thus need to have much faster reaction times producing hard, resistant, high mobility decoration. Traditional oleoresinous inks do not dry fast enough.

3.5.9 Printing in the round at about 800 cans per minute from a dry offset printing form necessitates that ink rheology must be controlled to minimise ink misting over a wide temperature gradient yet allow good flow on the can. This balanced rheology must allow for good lay on the can, producing a glossy result. The absence of a finishing varnish necessitates that the ink must also possess the barrier and mobility properties traditionally associated with a varnish.

3.5.10 Internal lacquers are sprayed into the DWI can and sometimes inadvertently impinge onto the external decoration. The ink must be resistant to the solvents present in the internal sanitary coating.

The now extensive use of DWI decorated beer and beverage containers in the open top market has developed to the extent that few cans for consumption in the UK (other than special sized cans such as airline packs) are now produced by flat sheet printing and subsequent welding or soldering.

Competition between tin-plated steel and aluminium still continues, but practical considerations of current filling-line handling are as important as any technical/commercial advantages of one type over the other.

## 4. General line printing

Traditionally the range of decorated containers and articles falling under the heading of general line work is extensive. A selection of general line products is listed below.

4.1	Paint cans	Sweet boxes
	Boot polish cans	Wastepaper bins
	Battery cases	Aerosol canisters
	Oil cans	Liquid cleaning containers
	Trays	Food cans
	Biscuit tins	Plant holders
	Processable food containers (e.g. pie cans)	

## 4.2 Ink requirements

Ink requirements for the general line area vary considerably depending upon the type of product in question. The average products require no more than the inks for the open top market described previously. Specific areas are:

### 4.2.1 General containers (and similar types)

Inks are printed onto either white enamel or sized metal. The main requirement is hardness and good tooling/adhesion properties.

#### 4.2.2 Processable food containers (e.g. pie cans)

As the decorated container will be subjected to aggressive processing (in-can cooking of contents), the decoration must not bleed under the high temperatures and steam contact involved. Temperatures of 120°C (steam at 15 psi) for 1.5 hours are normal.

Hardness and good tooling/adhesion are also of paramount importance.

### 4.3 Development areas for general line printing

Due to the wide area of product coverage in general line printing, developments have occurred more rapidly in certain product areas than others. These developments are now considered:

#### 4.3.1 Aerosol containers

The main development with aerosol containers is the rapid growth of the welded canister. The aesthetic appeal of the product has been markedly upgraded since the use of the welded container. The smaller aerosol container (e.g. spray perfumery) is basically a two-piece extruded container and is printed in the round in a similar manner (but at a much slower speed) to the DWI can. This type of container was basically the forerunner of the two-piece beer/beverage can.

#### 4.3.2 UV curing inks

The advantages found with UV inks in the open top market are also found for general line. Flexibility with interdeck drying, and cheap capacity expansion with interpass (set-stack) operations are the underlying reasons for the growth of UV in general line printing.

#### 4.3.3 Distort printing

In areas where the container is formed from a single flat sheet base (i.e. a drawn container) and the final product requires to be decorated, it is possible to take into account the degree of distortion over the whole container and graphically calculate the shape of the image required on the original flat sheet. The decoration thus takes on a "distorted form" which upon drawing results in an acceptable form. Distort printing is still in its early commercial phase, but improved quality and reduced costs could see expansion in this area.

#### 4.3.4 Drum printing

As in other areas of general line printing, the main change in drum printing is the growth of UV curing. The advantages found with UV curing applications are similar to those for general line printing and will not be considered any further here.

## 5. Other printing areas

### 5.1 Crowns and closures

Ink technology and printing technology have not changed much in the last ten years. Oleoresinous inks still have a major role to play.

#### *Ink requirements*

5.1.1 Excellent adhesion to the basecoat (enamel or size) is required to facilitate tooling. Tooling can be severe as

with Stelcaps and good adhesion is of paramount importance.

5.1.2 The ink must not be affected by high temperatures. The organosol lining compound applied to the inside of the crown is applied and stoved at 200°C. Any decoration must withstand this temperature.

5.1.3 UV curing inks have been tested for application to crowns but to date have not had the flexibility and tooling performance of oleoresinous products.

### 5.2 Miscellaneous printing applications

Each specialised miscellaneous application has its own printing ink requirements, some examples are:

#### 5.2.1 Dials and clocks

In this application adhesion and excellent light fastness are of paramount importance.

#### 5.2.2 Hacksaw blades

In this application the inks must be resistant to mineral oils and petroleum by-products as invariably the blades come into contact with these solvents.

#### 5.2.3 Extrusions (pen cases, toothpaste tubes, etc.)

Ink development in this area has mirrored that taking place in open top, in the sense that quick drying (DWI type) inks are finding wider application due to their toughness, good adhesion, etc. Product requirements are obviously similar to those of DWI containers. Ink rheology differs in that the presses are slower running and viscosities are somewhat higher.

## 6. Future developments

It will be obvious from reading this paper that a good deal of technology interchange has occurred in printing, in drying/curing and in ink systems between the various applications of container/article decoration. Efficiencies made in one area can sometimes be passed on to others and vice versa. Having seen the advances made, what about the future?

Any comments on future developments will inevitably contain an element of speculation and this should be borne in mind when interpreting the author's comments.

### 6.1 UV curing inks

It is anticipated that the growth of UV curing ink usage will continue, particularly in the general line and drum printing areas. Some UV introduction could occur in the DWI (two-piece can) printing area in a similar manner to the application already existing in the USA<sup>2,3</sup>. There appears to be little or no current growth in DWI metal decorating applications of UV curing in the USA, and any potential in the United Kingdom would have little or no technical or commercial advantage at this time.

### 6.2 Cheaper energy usage

Work has been continuing in the UK for some time to reduce energy requirements in metal decoration. It is likely that this investigation will continue with further developments of:

#### 6.2.1 Low energy coatings and inks



## 6.2.2 High solids coatings and inks

## 6.3 Water-based technology

Developments in water-based technology have not received the attention in the UK that has been paid in the USA. It is not thought likely that water-based coatings and inks will make a substantial impact in the foreseeable future.

Higher raw material costs together with energy costs to remove water have not helped the growth in usage of these products.

## 6.4 Expansion in the use of DWI ink technology

The development of fast curing, hard, lubricated inks for non-varnish application has already begun to grow. Lithographic application may follow with a potential expansion in the usage areas of these products. The potential of using lower energy with these inks is a possible further incentive to expand their use.

## 6.5 Metal decoration versus decorated "plastic" equivalent

The competition between the decorated metal product and

the decorated polymeric (plastic) equivalent product continues. Paint cans are a case in point. Many factors affect the choice between metal and plastic and the changes in those factors are difficult to forecast.

It is highly likely, for example, that aqueous-based paints will find a wider growth with plastic containerisation than with metal. The two packaging forms will, however, continue to fight for business share, with market share changing regularly as factors swing in different directions.

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# Quality control and standardisation in the titanium pigment industry

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## Summary

All manufactured products must be suitable for the markets for which they are intended. The International Organization for Standardization (ISO) is responsible for a wide range of specifications for both raw materials and finished products, and many national standards organisations adopt and sometimes adapt appropriate ISO standards for their own use.

It will be postulated that internal specifications are much more meaningful than those imposed by outside organisations. There are so many grades of titanium pigments available to the paint industry that it is difficult to see how they can be covered by a single specification. In the long run, it is the customer who will decide whether a product is satisfactory and specifications must accurately represent his needs. Thus, the best means of quality control is via specifications imposed either by the manufacturers or by their customers and mutually agreed. It can easily be demonstrated that improvements in raw materials have occurred partly because of competition within the industry and partly through customer demands.

## Introduction

In the hard commercial world the difference between success and failure depends on one's business being profitable. This means buying at a low price and selling at a high one, and in all companies a variety of other costs must be included in the equation that determines profitability. In simple terms we take raw materials, process them and make an end product which is then marketed.

In the titanium pigment industry the main raw materials are titanium bearing ore (ilmenite, slag or mineral rutile) and either sulphuric acid or chlorine and the product is a white pigment. In the coatings industry the starting point is pigment and resin (usually in solution) and the product is sold for application to a variety of surfaces which require protection and decoration. The variable costs to be added to raw material costs depend on the process but include energy and the cost of personnel necessary in the manufacture and marketing of the final product. In the latter sphere comes the quality control department, whose primary responsibility is to ensure that a product is suitable for the needs of the customer.

The mechanism by which this is achieved is the subject of this paper and it will be shown that product specification is a complex parameter involving many parts of a company. In the first place a manufacturer will usually have a range of products available, so that a potential customer can choose the most appropriate for his particular purpose. Technical representatives will assist him in making the right choice. To be more specific it would be useless to offer an anatase titanium dioxide pigment to a manufacturer of superdurable coil coatings, or a heavily coated pigment for use in glossy printing inks. Similarly a paint manufacturer would not provide a stoving lacquer to a man who wanted to paint his front door nor a matt latex paint for touching up his damaged motor car.

How, then, is suitability to be defined? Initially pigment

\*Paper presented at the Association's York Conference, 15-18 June 1983. An edited transcript of the discussion that followed this paper can be found on page 317.

manufacturers produce grades that are recommended for a variety of applications, and by a combination of customer preference and manufacturing skill on the part of raw material suppliers a successful product range is achieved.

### The need for quality control

In any manufacturing process, particularly those involving chemical and physical reactions, the properties of the final product will cover a range of values. To quote a simple example, titanium pigment manufacturers attempt to produce pigment particles of a specific size. In this way optical properties, particularly opacity, are maximised and any departure from the optimum size represents a loss of opacity. The mechanisms of crystal growth, however, whether in a calciner (for the sulphate process) or a reactor (for the chloride process) are such that it is inevitable that a range of sizes will be produced. The skill of the pigment maker is in restricting the size distribution as far as is practicable. This demands a high degree of control over the physical processes involved, usually by rigorous temperature control and the judicious use of growth control agents.

The same reasoning can be applied to most products, and in the field of coloured surface coatings an *exact* colour match is not always achieved. In some areas, for example decorative paints, the ultimate is not even necessary and it is up to the supplier and purchaser to set up tolerances that are adequate for both their purposes. The important point is that both needs must be satisfied: quality control is expensive and is an appreciable part of manufacturing costs. Thus on economic grounds it needs to be simple and rapid, but at the same time meaningful and effective. It is a matter for discussion as to whether purchasers of raw materials should carry out quality control on receipt or whether they should rely on their suppliers. If they are to be expected to carry out any testing what should they do? And how often? It has been said on many occasions that industry will accept any test as long as it is quick and cheap, and that is a view that can be sympathised with. An equally simplistic view is that a paint manufacturer does not buy pigment in order to test it but to put it into paint.

The one thing that is certain is that an unreliable product will not sell in a quality conscious market place, and the advent of the Sales Description Act and similar legislation has persuaded all suppliers that some sort of guarantee of quality is essential.

### The International Organization for Standardization (ISO)

With increasing international trade there is a need for standards of manufacture that are recognised all over the world, and the aim of ISO is to provide such a framework. Industry as a whole has been divided into appropriate sections, and specifications for thousands of products, together with test methods for their evaluation, have been drawn up. Unfortunately not every country is active in every sphere, either on the grounds of expense or because of lack of interest in a particular field. Thus involvement on an international scale tends to be rather limited. The countries that are active in ISO Technical Committee TC35, which deals with paint and allied products and their raw materials, are the following:

Belgium, Brazil, Canada, China, Dominican Republic, Egypt, France, Germany, India, Iran, Ireland, Israel, Italy, Kenya, Netherlands, Norway, Poland, Portugal,

Romania, South Africa, Sri Lanka, Sweden, Switzerland, UK and USSR.

It will be seen that there is strong support from Europe, and indeed the secretariat is held by the Netherlands, but notable exceptions are the USA, who withdrew in 1977 following lack of agreement between ASTM and ANSI, their two standards organisations, and Japan. The United Kingdom is active in all parts of TC35 and holds the secretariat of SC9 – the sub-committee dealing with Test Methods for Paints. The pigment sub-committee SC2 is run by Germany with active support from Belgium, Canada, France, Iran, Netherlands, Norway, Romania, South Africa and UK. With the exception of Iran and Romania all these countries manufacture titanium pigments and have an obvious concern for specification and test methods for that product. Again there are notable omissions which have major producers of titanium dioxide.

Originally, titanium dioxide had its own sub-committee, SC4, but since 1980 all pigment matters have been dealt with by SC2 constituted as described above. Titanium dioxide has been discussed at four international meetings (either of SC4 or SC2) and a specification ISO/R798 was first produced in 1967. It was revised in 1977 as ISO 591 to include heavily coated pigments primarily intended for matt emulsion paints since these were not included in the original classifications.

So, what has this international committee produced as a specification for titanium dioxide for paints? Firstly, it recognises that there are two basic crystal forms – anatase and rutile – though the former is rarely seen in modern paint formulations. Secondly, it acknowledges that surface treatments, of other inorganic oxides, are applied to many commercial products to improve durability and dispersibility. In the case of anatase, two grades are specified, A1, with a TiO<sub>2</sub> content of at least 98 per cent, and A2, with a minimum TiO<sub>2</sub> level of 92 per cent. For rutile pigments, three grades, R1, R2 and R3, with minimum TiO<sub>2</sub> contents of 97, 90 and 80 per cent respectively, are included. Thus there are five categories of titanium dioxide for paint in the current International Standard. There are 35 companies manufacturing titanium dioxide throughout the world, producing between them about 600 different grades, 375 of which could be recommended for use in paint. Table 1 shows the distribution of these in terms of ISO 591.

Table 1  
Number of titanium dioxide grades for paint

A1	A2	R1	R2	R3
47	39	24	205	60
86 (23%)		289 (77%)		

It will be no surprise that more than three-quarters of these grades are rutile nor that 70 per cent of the rutile grades fall in Grade R2, and in terms of sales volume grades R2 and R3, constituting respectively 77 per cent and 22 per cent of the titanium pigment sold for paint manufacture, are overwhelmingly dominant. Thus in practice only two of the five grades specified in ISO 591 are relevant to modern paint manufacture, and within both of these groups there is a wide range of properties. R2 for example includes pigments that could be described as semi-durable, durable or even super-durable, and the

Table 2  
Typical analysis of Tioxide Grade R2 pigments

	Min	Max
Al <sub>2</sub> O <sub>3</sub> content (%)	1.8	5.5
SiO <sub>2</sub> content (%)	0.1	2.5
TiO <sub>2</sub> content (%)	90	95

coating levels of alumina and silica are equally variable as Table 2 shows.

Since the properties of pigments are significantly affected by the surface treatments applied, it will be obvious that considerable variation in durability, dispersibility and optical properties will exist within this single category. Similar wide ranges appear in R3, which includes both pigments designed for use in matt emulsion paints and some super-durable pigments where the heavy coating is designed to restrict the photoactivity of the pigment.

The primary purpose of a specification is to ensure consistency of performance rather than to compare one product with another. So once a sample has been approved all that is necessary is to ensure that future deliveries are similar to this approved standard sample. Thus in most specifications there are two types of requirement: there are properties to which numerical limit values are assigned, where it has been established that such values are both relevant and realistic, and other tests where a simple comparison with the standard is sufficient. In ISO specifications these two requirements will in future be separated into "defined" and "agreed" characteristics. Table 3 shows the defined characteristics from ISO 591 together with the values assigned for each grade, while Table 4 lists the properties whose values are to be agreed between purchaser and vendor via a standard sample. In all cases appropriate ISO test methods are specified.

Table 3

Characteristic	Requirements for				
	Type A		Type R		
	A1	A2	R1	R2	R3
TiO <sub>2</sub> content, % min	98	92	97	90	80
Matter volatile at 105°C at point of acceptance, % max	0.5	0.8	0.5	to be agreed	
Matter volatile at 105°C after 24h preconditioning at 23 ± 2°C and 50 ± 5 % RH, % max*	0.5	0.8	0.5	1.5	2.5
Matter soluble in water, % max	0.6	0.5	0.6	0.5	0.7
Residue on sieve, 45µm, % max	0.10	0.10	0.10	0.10	0.10

\*Only applied if specified by interested parties or in a contract.

Table 4

Colour
Lightening power
pH of aqueous suspension
Oil absorption
Resistivity of aqueous extract (for A2, R2, R3)

## National specifications

Member bodies of ISO are committed to adopt ISO specifications and test methods unless they have opposed them at the final voting stage. Thus France (NF T31-010), Germany (DIN 55912) and the United Kingdom (BS 1851) have issued specifications for "Titanium dioxide pigments for paints" that are technically identical with ISO 591. No further comment on these is therefore needed.

Standardising bodies in other countries have not yet adopted ISO 591 and the current standards of a selection of these will be presented for discussion.

### (a) USA (ASTM)

The first specification for titanium dioxide produced by the American Society for Testing of Materials was issued in 1938 and must have been the first ever. D476 has been revised several times since that date with the last revision in 1973. It has been adopted by the American National Standards Institute as ANS K45.1 and is a remarkably simple document. Four types of pigment are recognised and are defined in terms of their use as well as by their TiO<sub>2</sub> contents. They are as follows:

- Type I Anatase-Free Chalking – white exterior house paints; interior uses. Minimum TiO<sub>2</sub> content = 94 per cent.
- Type II Rutile – Medium Chalk Resistant – low-medium PVC enamels and lacquers. Minimum TiO<sub>2</sub> content = 92 per cent.
- Type III Rutile – Medium Chalk Resistant – medium-high PVC enamels. Alkyd and emulsion flat wall paints. Minimum TiO<sub>2</sub> content = 80 per cent.
- Type IV Rutile – Highly Chalk Resistant – exterior coatings requiring excellent durability and gloss retention. Minimum TiO<sub>2</sub> content = 80 per cent.

It will be noticed that the ISO grades A1 and A2 are covered by Type I, not unreasonably since neither grade enjoys significant usage. The distribution of rutile grades is more difficult to recognise, with the exception of Grade R3 which clearly agrees with Type III. A Grade R2 pigment could be either Type II or Type IV depending on its durability, but there is no clear indication of what is meant by "highly chalk resistant". The definition of chalk resistance in the standard recommends "that purchaser and seller agree upon standards and methods of test suitable for their requirements". A pigment manufacturer may have some difficulty in categorising all his products in a way that satisfactorily differentiates between them. Pigments designed for super-durable applications such as automobiles and coil coatings for sidings are more durable than those necessary for exterior decorative paints; the latter are in turn more durable than those recommended for domestic appliance finishes. Perhaps the next revision will include Type V in order to accommodate super-durable pigments which currently can only be included in Type IV alongside highly chalk resistant grades.

The only other features of ASTM D476 are the specification of:

1. Matter soluble in water (via specific resistance of an aqueous extract).

2. Moisture and other volatile matter (loss at 105-110°C, after preconditioning for referee purposes).
3. Specific gravity.
4. Coarse particles (residue retained on 45µm sieve under specified conditions).

The specifications for specific gravity are worthy of comment: the acceptable range for Type I (anatase) is from 3.8 to 4.0. Thus coated pigments, which typically have densities of 3.7, are excluded; moreover since pure anatase has a density of 3.85 (to the nearest 0.05) it is difficult to see how a density in excess of this could be achieved when all the additives used are less dense than titanium dioxide. The range for Type I should more realistically be 3.7-3.9, but with present day pigments, density can no longer be used to differentiate between the various types.

#### (b) Spain

There are two specifications for titanium dioxide, UNE 48044 for anatase, and UNE 48178 for rutile. Both are long overdue for revision having last been amended in 1965 and 1963 respectively. The government department that issues quality and composition certificates for paints and raw materials has its own specifications but for titanium dioxide usually applies ASTM D476; there are no plans at the moment to bring the INRANOR (Instituto Nacional de Racionalisacion y Normalisation) standards up to date.

More information is called for than with either the ISO specification or ASTM D476 and the defined characteristics are summarised in Table 5.

Table 5

	UNE 48044 anatase	UNE 48178 rutile
TiO <sub>2</sub> content, % min	96	96 (normal) 94 (chalk resistant)
Water-soluble matter, % max	0.5	0.5
Moisture content, % max	0.5	0.5
Iron content, % max (as Fe <sub>2</sub> O <sub>3</sub> )	0.012	0.009
Silica content, % max	0.10	0.1 (normal) 1.0 (chalk resistant)
pH	7-8	7-8
Lightening power, min	1175	1500
Oil absorption	32	52±6
Agreed characteristics are colour (dry) and colour (in oil).		

#### (c) Belgium

The Belgian standard NBN T21-101 is currently in preparation, but the discussion document closely follows ISO 591. Thus it is only necessary to mention those parts that differ from the ISO specification.

Two omissions are the matter soluble in water and the sieve residue, while the anatase content of rutile pigments and the amount and nature of surface treatment are both to be the subject of agreement between interested parties. These last two added qualities are both important in determining the final properties of the pigment in practical use,

with particular regard to durability, which can obviously not be tested directly before pigment is sold.

#### (d) Japan

JIS K5116-1973 was confirmed in 1979 and is still considered to be relevant. There is no reference to ISO and the test methods involved are all included in JIS K5101 – 1964 (re-affirmed 1968) – Testing Methods for Pigments.

Six types of pigment are classified according to the main components of the treatments applied and by minimum TiO<sub>2</sub> content, as shown in Table 6.

Table 6

	Treatment	TiO <sub>2</sub> content, % min
Anatase class 1	none	98
Anatase class 2	Al	95
Rutile class 1	Al	92
Rutile class 2	Al, Si	92
Rutile class 3	Al, Si, Zn or Al, Zn	92
Rutile class 4	Al, Si	82

The relationship between this classification and that of ISO 591 is by no means clear. Anatase class 1 is the same as Al, and class 2 is similar to A2, while rutile class 4 is similar to R3; but rutile classes 1-3 would all be included in ISO's R2. R1 – untreated rutile – does not appear at all, though from the sales statistics recorded earlier this is obviously no great loss.

The defined characteristics demanded are similar to those of the ISO specification, but there are differences in the limit values as shown in Table 7.

Table 7

	Anatase		Rutile			
	1	2	1	2	3	4
Residue on sieve, % max	0.2					
Volatile matter, % max	0.7		1.0			2.5
Water-soluble matter, % max	0.5					
pH	6-9		6-8			6-9

A point in favour of the Japanese specification is that an attempt has been made to evaluate properties that have relevance to the practical use of the pigment. Thus as well as tinting strength (lightening power), hiding power is evaluated, in addition to sieve residue there is reference to dispersion, and oil absorption is supplemented by "fluidity". Unfortunately the medium recommended is not often used in modern paint manufacture. Pigment is dispersed in boiled linseed oil using an automatic miller to produce a paste which is tested for colour, hiding power, dispersion (via fineness of grind) and fluidity. By a coincidence the fluidity test described in JIS K5116 is also used in the routine testing of artists' liquid colours, where it has relevance to the application properties of the paint. In the Japanese specification fluidity is evaluated for



Table 8

Characteristic	ISO	ASTM (USA)	INRANOR (Spain)	IBN (Belgium)	JIS (Japan)	ISI (India)
No. of grades (anatase/rutile)	2/3	1/3	1/2	2/3	2/4	1/3
TiO <sub>2</sub> content	D	D	D	D	D	D
Volatile content at point of acceptance	D		D	D	D	D
Volatile content on conditioning	D	D		D		
Water-soluble content	D		D		D	D
Sieve residue	D	D			D	D
Fe content			D			
SiO <sub>2</sub> content			D			
pH of aqueous extract	A		D	A	D	D
Lightening power	A		D	A	A	A
Oil absorption	A		D	A	A	D/A
Colour (dry)			A			
Colour (in oil or paint)	A		A	A	A	A
Resistivity of aqueous extract	A	D		A		A
Anatase/rutile ratio				A		
Coating levels				A		
Specific gravity		D				
Chalk resistance		A				A
Hiding power (in oil or paint)					A	A
Dispersibility					A	A
Fluidity					A	
Water demand						A
No. of characteristics (defined(D)/agreed(A))	5/5	5/1	8/2	3/7	5/6	6/8

pigment pastes prepared with a printing varnish, recognising the importance of flow properties in the printing ink industry.

#### (e) India

Indian Standard IS:411-1968 : Titanium dioxide for paints originally referred to both anatase and rutile types in the same document, but has now been reprinted in two separate parts – IS:411-1981 and IS:9788-1981 dealing with anatase and rutile respectively. In the specification for rutile pigment the three grades are as in ISO 591 and most of the properties tested are those specified in ISO 591, though the limit values are not always the same. The main attraction of IS:9788 is in its genuine attempt to relate to practically significant pigmentary properties and to relevant paint formulations. It is not completely successful – pigment purchasers will not usually have time to examine chalk resistance and durability (even by accelerated weathering) before they use the pigment, and pigment manufacturers could not reasonably be expected to examine these properties before releasing pigment for sale. However the use of a high speed impeller mill for evaluation of dispersibility is completely in line with the current practice of pigment makers, and the determination of opacity in a paint is also to be encouraged. Colour and tint reduction (lightening power) are also evaluated in paints.

One of the declared aims of the new Indian standard was to use objective tests rather than subjective ones and to avoid as far as possible comparisons with an agreed sample. If it is accepted that the main purpose of quality control is to ensure consistency the philosophy of matching the performance of an agreed sample can hardly be faulted. It is more important to use tests that are meaningful in terms of the final application of the product.

#### (f) General discussion on national standards

Comparison of the standards mentioned above shows that quite wide variations exist both in the scope of testing and methods of evaluation, and Table 8 summarises the properties tested and whether the test gives a defined value or is simply comparative. It will be seen that the only characteristic that is common to all the specifications considered is the analysis for titanium dioxide content, which is used for classifying the various grades. As has been discussed above, the value of the classifications chosen is questionable since most grades used commercially in the paint industry fall into one or two categories. However, different parameters have been used to establish categorisation: ISO uses primarily TiO<sub>2</sub> content, ASTM concentrates on durability, and JIS refers principally to coating composition; when the limiting titanium dioxide concentrations are superimposed on these parameters, confusion exists. Using some grades manufactured by Tioxide UK Ltd as examples it can be shown that pigments can change groups depending on the specification referred to. Table 9 summarises the situation.

It is easy to see the anomalies. In the ISO and ASTM systems Tioxide R-XL and Tioxide R-TC50 are in a class apart from the other grades, but in JIS they are included with a super-durable and a general purpose durable grade (R-TC60 and R-TC4 respectively). Tioxide R-TC4 and Tioxide R-CR2, on the other hand, although very similar both in application and properties fall into different groups in JIS because of the presence of zinc in Tioxide R-CR2. The reader is left to perform the exercise with Tioxide R-HD2 and Tioxide R-TC90, which are also similar in performance but differ in the method of manufacture.

There are two reasons for the specification of volatile content: firstly, its determination at the point of

Table 9

Pigment	% TiO <sub>2</sub>	ISO	ASTM	JIS
Tioxide R-CR2 – general purpose, durable	93	R2	IV	R3
Tioxide R-HD2 – high gloss	94	R2	II	R2
Tioxide R-TC4 – general purpose, durable	90	R2	IV	R4
Tioxide R-TC90 – high gloss	94	R2	II/IV	R1
Tioxide R-XL – matt latex paints	80	R3	III	R4
Tioxide R-TC50 – latex paints	88	R3	III	R4
Tioxide R-TC60 – super-durable	91	R2	IV	R4

acceptance, i.e. at the customer's premises, will establish whether the pigment has been exposed to excessive moisture in transit, and secondly, determination of volatile content after pre-conditioning will give some idea of the physical and chemical properties of the pigment surface.

In common with most fine powders, titanium dioxide will absorb or adsorb moisture from the atmosphere in proportion to the relative humidity. Grades with surface treatments of silica and alumina are particularly sensitive, and generally speaking the greater the level of coating the more rapidly moisture will be adsorbed, both physically and chemically. Thus every grade has an equilibrium level of moisture under ambient conditions. In practice, a certain proportion of moisture is essential for surface treated titanium pigments to achieve both satisfactory ease of dispersion and optical properties; completely dry pigment will sometimes be found to give inadequate performance. Fortunately such occurrences are rare since the time between packing and usage of pigment is normally sufficient to allow the adsorption of the minimum moisture content required.

It is obviously undesirable, however, for pigment, usually packed in paper sacks, to be subjected to heavy rainfall: wet lumps will be difficult to handle and will not disperse satisfactorily. The situation may be exacerbated if the wet pigment is allowed to dry out, for it will then assume the form of very hard compacted pieces varying in size from 1-100 mm in diameter. These will be difficult to disperse in any system and with any type of milling equipment. Most pigment manufacturers now provide plastic shrink wrapping round each 1 tonne pallet so that excessive moisture pick-up cannot occur.

So, the provision of a specification for maximum moisture content on delivery ensures that the manufacturer provides effective packaging of his product, while the requirement for examination after pre-conditioning assists in establishing that the surface characteristics of the pigment have been reproduced.

Matter soluble in water, whether determined directly or via resistivity of an aqueous extract, figures in most of the specifications. Its importance is its probable connection with corrosion resistance, dispersibility and dispersant demand, and adhesion, particularly intercoat adhesion, though not all of these properties will be important in many cases. Paint makers have an instinctive dread of pigments with high soluble salts especially in industrial and automotive applications, though little work seems to have been carried out to establish an acceptable level. The maximum values quoted in the specification, approximately 0.5 per cent appear to be reasonable.

There is some doubt about the reason for quoting sieve residue, and most technologists would suggest a connection between it and dispersibility. Hard large particles

would be expected to be difficult to disperse in paint making machinery, but examination of the specifications shows that various tests employing different intensities of dispersion before passing a slurry through a sieve are available. ISO/591 employs a mechanical sieving device which imparts substantial dispersive forces to the pigment before it is sieved and it would be surprising if any titanium dioxide particles remained on a 45µm sieve. This test therefore is primarily looking for extraneous matter such as fibres and other accidental contamination. The ASTM, JIS and ISI tests on the other hand assist the passage of pigment, sometimes pre-dispersed in water, through the sieve by means of a soft camel hair brush. Two critical factors are the way in which the initial dispersion is made (type of stirrer, speed of rotation, pigment concentration) and the vigour with which the pigment is brushed on the sieve. It is more likely with these tests that pigment particles will be retained on a 45µm sieve but by no means certain that they will cause problems in paint manufacture, since it is their hardness that will determine dispersibility, in combination with the efficiency of the milling equipment.

Both the Japanese and Indian specifications attempt to evaluate dispersibility of pigment by actually milling pigment in a medium. Of the two the Indian proposal is the more practical since it requires the use of equipment that is similar in design to paint making machinery. The Japanese method specifies an automatic miller and a fairly viscous millbase, attempting to simulate conditions appertaining in, for example, a three roll mill. For modern titanium pigments the automatic miller is quite insensitive under the conditions specified and even samples that have been found to be difficult to disperse by other means will disperse satisfactorily. Another disadvantage is that the medium specified – boiled linseed oil – will have quite different wetting characteristics from the vehicles used in paints. The Indian method, on the other hand, suggests the use of an alkyd resin with a high speed impeller mill.

At this point it is relevant to mention other work that has been, or is being, carried out in ISO. In particular there is now a working group looking into the evaluation of dispersibility in general and it is hoped that eventually some of the products of this group will find their way into pigment specifications. The basis of the scheme that is being considered is that the evaluation of dispersibility involves a number of parameters, namely:

1. Type of milling machinery and millbase composition.
2. Type of milling medium.
3. Method of assessment of dispersion.

So, a modular system has been devised whereby these parameters are selected to suit particular pigments and applications. At present the only approved system is the German DIN 53238 and this is being considered and enlarged before being issued as an ISO specification.

There is, in fact, already one ISO method for evaluation of ease of dispersion – ISO 787/Part XX – based on a mechanical shaker and this will form part of the general method under discussion. Other parts may include a high speed impeller mill and an automatic muller, while amongst the methods for assessment will be fineness of grind, gloss measurement and tinting strength (for coloured pigments). As the specification of resin systems is extremely difficult it is probable that the choice of medium will be left to agreement between interested parties. The method proposed in the Indian standard could form part of the ISO specification or alternatively, and preferably, be replaced by the latter in due course.

After ease of dispersion, it is debatable whether colour or opacity is the more important property of titanium dioxide and it is therefore surprising that neither of these appears in any form in the ASTM specification. Colour of the dry powder is omitted from most specifications, as it is not always reflected in the colour of pigmented resin, though the test itself can be carried out quickly and has merit in some situations. Apart from ASTM all the specifications considered call for colour in a medium to be similar to that given by a standard sample. Again the Indian specification is the only one that requires the testing of a paint, and a formulation for a typical alkyd gloss paint is given; the other methods all rely on a paste in oil.

Opacity has been traditionally related to lightening power (or tinting strength as it was originally and erroneously designated), but it is not difficult to find examples where lightening power in castor oil (by ISO 787/Part XVII) does not correspond to opacity. A simple case is where pigments are designed for use in paints with high total pigment volume concentrations and rely partially on dry hiding for their opacity: in ISO these are covered by Grade R3. However lightening power, in its usual form, appears in all the specifications and only Japan and India have attempted to examine the opacity of a white pigmented system. JIS K5116 uses the same paste as was prepared for colour comparison and applies it over a chequer board hiding power chart, looking for the contrast between black and white areas of the chart. The Indian specification also requires use of a hiding power chart but makes the comparison between sample and standard via the alkyd paint mentioned already. The intrinsic hiding power of a pigment will depend on the medium in which it is dispersed and on the efficiency and stability of dispersion, so it might be questioned whether this property can be adequately characterised. Nevertheless, accepting the shortcomings of testing in a single medium, it does seem preferable to relate to an alkyd resin rather than a relatively simple oil that has little practical significance. It is also necessary to specify the film thickness at which opacity is to be determined, and the most recent methods for paint testing refer to a constant spreading rate of  $20\text{m}^2/\text{l}$ .

Similar reasoning can be applied to the evaluation of oil absorption, a property that is considerably affected by the acid value of the oil used. Generally speaking, the lower the acid value the greater will be the determined oil absorption. Extending the argument to the wide range of media used in paint manufacture, not excepting variation of solvent, oil absorption becomes of little import. A more worthwhile property would be medium demand, for solvent-based systems, or dispersant demand for aqueous systems, but no official specification has yet included either of these. The nearest specified property in this area is water demand, in the presence of dispersant, which appears in IS:9788.

To summarise, it is obvious that there are considerable

differences between the specifications in existence in different parts of the world. They range from rather simple documents with a limited number of tests that are not always directly relevant to the final use of the pigment, to more comprehensive standards with more tests that attempt to be practically significant. Reverting to the primary requirement for a specification – to ensure consistency of quality rather than to compare different products – any of the standards discussed could be used. The important question is whether two samples of a particular pigment could perform differently in a practical situation and yet be indistinguishable when tested according to a specification. The answer must be in the affirmative, and consideration of the ISO specification implies that there is no indication of ease of dispersion except in the form of a sieve residue test. As paint making machinery has become more demanding of pigmentary properties such as wetting and dispersion, the physical chemistry of the pigment surface has become more and more important. Simply to state that a pigment is coated with alumina and silica, even if the proportions are known, is no guarantee of pigment performance and much expertise is involved in the precipitation of these coatings on to the titanium dioxide. Thus it is necessary to have tests that relate to a practical situation, but yet that are not too specific.

### Internal quality control

Once a pigment has been manufactured there is little that can be done to it to change its quality. All that a manufacturer can do is to pack it carefully and ensure as far as possible that it is protected from harmful environments, such as one with excessive moisture, so that its initial properties can be preserved. Thus the testing that is carried out on a titanium pigment in its manufacturer's control laboratories can only be confirmatory. A pigment sample meets a specification or it does not and although information of this nature can be used to control the properties of future production, what is generally described as quality control is more accurately "categorisation".

The control over the quality of titanium pigments is exerted during their manufacture and a glance at a simple flow sheet of the process will suffice to indicate how many points there are where important checks and adjustments can be made. Figure 1 is a schematic diagram of the sulphate process for the manufacture of titanium dioxide pigments, with asterisks representing the numerous points in the process when some form of operational control is carried out. The sulphate process is said to make use of all the processes of classical chemistry except distillation. In principle the process is simple, initially requiring the solution of ground ilmenite, or titanium slag, in sulphuric acid. Impurities are removed and titanium dioxide is precipitated from the liquor. The precipitate is washed and then calcined to enable the crystals to grow to the optimum size for scattering light. Surface treatments, usually in the form of alumina and silica, are applied to the pigment surface by precipitation and the pigment, after final washing, is eventually micronised and packed.

At all the stages of the process relevant testing is carried out, starting, for the sulphate process, with analysis of the ore in order to determine the strength and quantity of sulphuric acid needed for digestion. Particle size of the ground ore is controlled by an air flotation technique, this being particularly important in establishing the best conditions for solution. The mixture is heated with steam and at about  $160^\circ\text{C}$  a violent exothermic reaction occurs resulting in a porous cake containing ferric, ferrous and

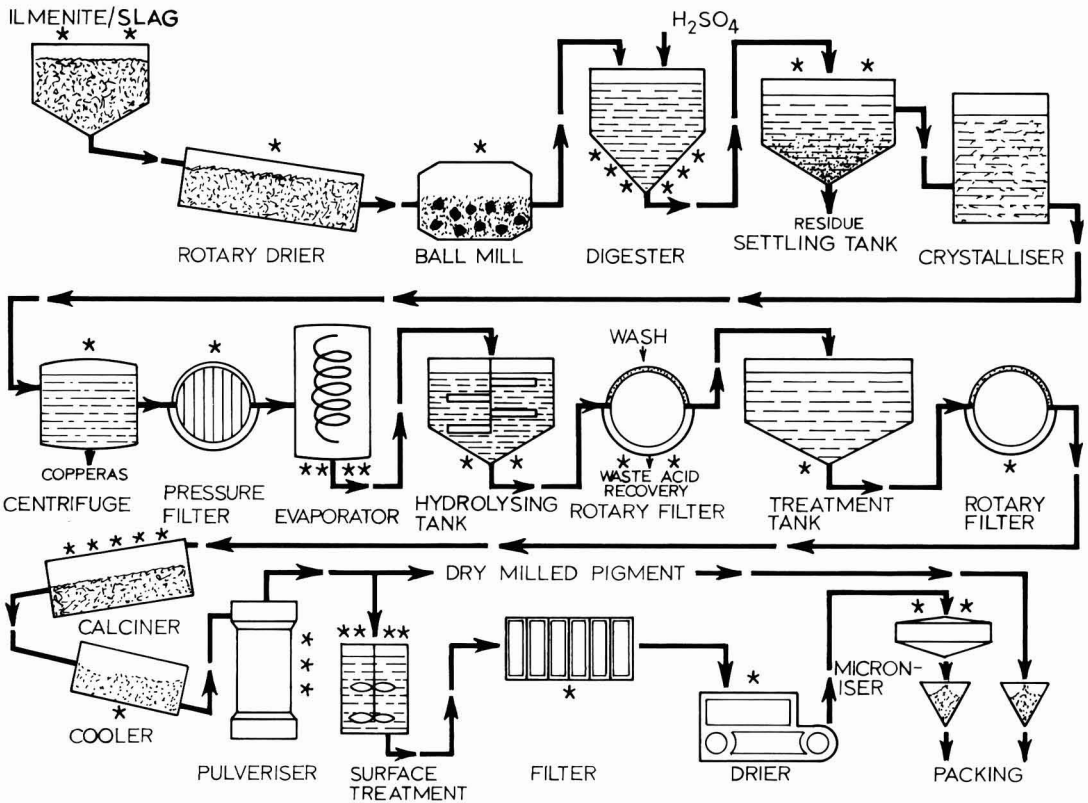


Figure 1. Diagrammatic representation of the sulphate process for manufacture of titanium dioxide pigments. Asterisks denote the points where and the degree to which information is used to control the process

titanium sulphates. This is extracted with water or dilute acid and the ferric iron is reduced to the ferrous state by means of scrap iron. Reduction is carried to the point where some trivalent titanium is present in order that all the iron remains ferrous during subsequent handling.

Most of the insoluble residues are removed by settling, which is aided by the addition of flocculating agents, and ferrous sulphate is crystallised by cooling to about 10°C and centrifuged out of the liquor. The last traces of sludge are removed by filtration.

Concentration of the solution to a specific gravity of about 1.67 at 25°C results in liquor containing about 230g/l of TiO<sub>2</sub>, if ilmenite was the starting material. Precipitation of hydrous titanium dioxide is the most critical stage of the whole process and it is essential that no ferric iron is present. The precipitation must be carried out under rigidly controlled conditions so that the precipitate can be readily filtered and washed, and also, on subsequent calcination, give crystals of the desired type and size. It is possible to obtain a precipitate by simply boiling the solution, but in practice seeds known as nuclei are added to encourage the correct formation. Nuclei are prepared from pure titanium tetrachloride solution by partial neutralisation and heat treatment. Whether anatase or rutile pigment is eventually to be produced is determined by the manner in which the nuclei are prepared, and the quality of the precipitate depends on the composition of the main solution and that of the nuclei as well as on the duration of

boiling. An interesting point is that the precipitated titanium dioxide is always in the anatase form and the type of nuclei is only effective during calcination, where the final form of the pigment is determined. During the washing of the precipitated pulp it is essential to ensure that it is free of adsorbed iron, which would have a deleterious effect on the colour of the pigment.

Calcination is carried out in internally fired inclined rotary kilns, through which the pulp moves slowly under gravity. On its way through the kiln the pulp is first dried and sulphate ions are driven off. Conversion to rutile and crystal growth only occur as the end of the kiln is reached where the temperature is of the order of 1,000°C, varying according to the grade being produced. Conversion to rutile is governed primarily by the amount of nuclei added at precipitation and small additions of, for example, potassium salts, phosphate and zinc or aluminium made to the pulp immediately before calcination control crystal growth. After cooling, the pigment may be milled and sold as a dry milled, untreated product but most production is surface treated to improve optical properties, dispersibility and durability.

Surface treatment involves the formation of a coating over the surface of the pigment particles. The coating agent must be a colourless hydrous oxide, silica and alumina being commonly used, but others, including titania and zirconia, are used for particular purposes. It is first necessary to ensure that the pigment is well dispersed,

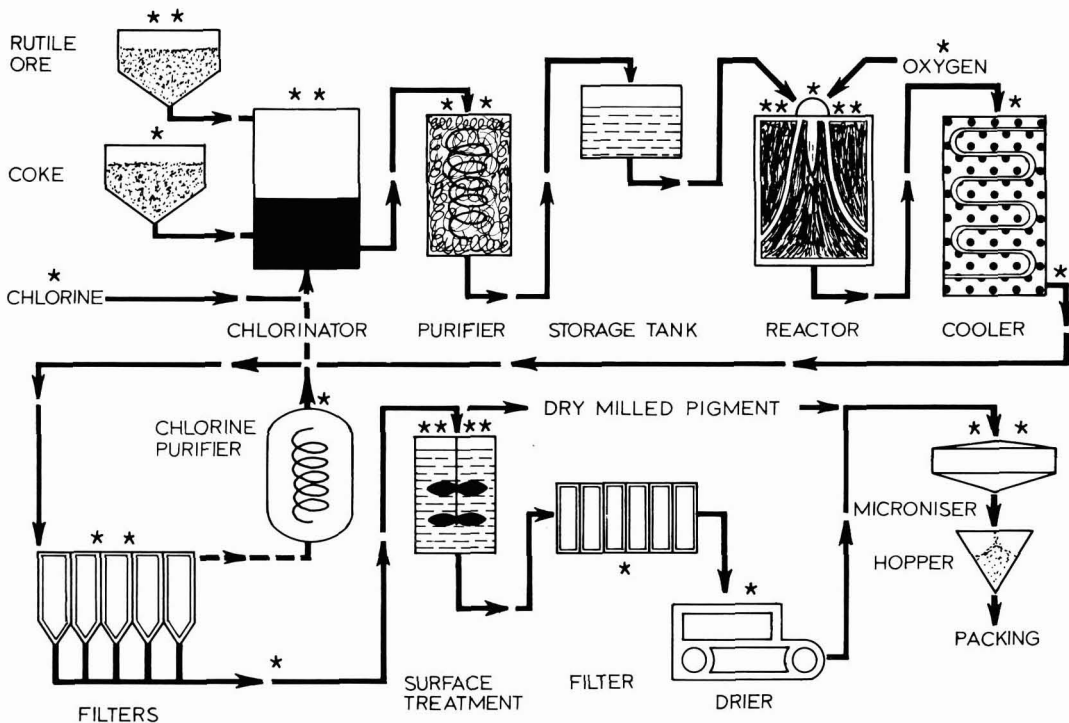


Figure 2. Diagrammatic representation of the chloride process for manufacture of titanium dioxide pigments. Asterisks denote the points where and the degree to which information is used to control the process

usually by sandmilling, to ensure that any over-sized particles consisting of sintered aggregates are eliminated. The coating reagents are added to the slurry which is continuously agitated, and exact control of pH ensures that coatings are precipitated on to the pigment surface in the correct sequence and in the desired form. There are numerous references to coating compositions and techniques in the patent literature, all drawing attention to the precision required at this stage of the process.

The final milling of the pigment is carried out after drying to a specified moisture content and normally takes place in some form of fluid energy mill such as a microniser. The ratio of pigment to steam and the rate of feeding are obvious controlling factors in the efficiency of milling and it is common to add organic compounds to improve milling efficiency as well as to assist the dispersing properties of the pigment when it is eventually used.

It is obviously impossible in the present paper to describe all the points in the process where controls and checks are made. The frequency of asterisks in Figure 1 gives some idea of the number of data points that go towards ensuring the quality of the final product. As was stated at the beginning of this section, testing of pigment is largely performed in order to confirm that its quality is as expected.

Figure 2 is a similar diagram representing the chloride process, where again the basic chemistry is fairly simple. Mineral rutile is chlorinated in the presence of coke, the resulting titanium tetrachloride is purified by distillation and then oxidised to titanium dioxide pigment. Thereafter

the process is similar to the sulphate process, pigment being coated and finally micronised.

### Manufacturers' specifications (categorisation)

Though this paper refers in its title to "the titanium pigment industry", it will be obvious that the author's knowledge of manufacturers' specifications is limited to a single company. Thus this section will refer specifically to Tioxide UK Limited, but in the expectation that other manufacturers operate in a similar manner.

The advantage that a manufacturer has over a standardisation organisation is that he knows his own products and therefore recognises their important properties. He is not restricted to general classifications and every grade that he produces has its own specification. So he can choose tests that are appropriate to the specific applications of the pigments: products for use in printing inks can be tested in an ink formulation and evaluated for suitable properties such as opacity and gloss at a low film thickness; products intended for water-based paints will be tested in aqueous systems. At the same time certain tests will be performed that are known to relate to practical situations but in themselves do not directly simulate realistic conditions.

Testing carried out in the Control Laboratories of Tioxide UK Limited may be divided broadly into analysis and performance, and since individual pigments are made to a specific formula, suitable tolerances for chemical composition can be established. Thus all coated rutile grades (i.e. grades R2 and R3 in ISO 591) are analysed for



alumina and silica content. It is fitting to note here that aluminium in a pigment may be present either in the crystal itself as a deliberate addition or as part of the pigment coating. A simple determination of the aluminium content will not establish the location of the element and therefore cannot be used to predict the properties of the pigment. So the use of treatment elements to categorise pigments (as in the Japanese JIS K5116) could be quite misleading. Analysis for aluminium and silicon, and for zinc also if appropriate, is carried out by X-ray fluorescence using automated equipment dedicated to the assay of specified elements. In certain cases these may include elements that impart special properties, for example, zirconium, which is an important component of some pigments intended for super-durable applications. Determination of heavy metals content such as lead is necessary for pigments that are to be used as food additives, though all TiO<sub>2</sub> grades are suitable for use in paints for toys, food factories, catering establishments etc., and in papers and inks for food wrappings.

An important feature for the pigment manufacturer, and ultimately for the consumer, is the efficiency of rutilisation in rutile pigments, which has relevance to the ultimate durability of a pigment. Equally with anatase pigments it is essential for some non-paint applications that the rutile content is kept to a minimum. The ratio of anatase to rutile is checked by X-ray diffraction. The only national specification that mentions this property is NBN T21-101 from Belgium, where similarity to an agreed sample is specified.

Soluble salts, usually determined from the conductivity of an aqueous extract, and pH are evaluated for all pigments and give an indication that the washing of the pigment has been carried out effectively. This is important for many applications, particularly those based on water, where variation in soluble salt content, and/or pH, could affect the amount of surfactant necessary to disperse the pigment. Practically all the specifications discussed earlier include both these parameters, but whereas the same limit values are quoted for all grades, a pigment manufacturer will set standards appropriate to individual pigments. Similarly moisture content (loss at 105°C) does not normally pose a problem in a pigment warehouse, since the pigment is warm and dry when it is packed and most grades are now shrink wrapped with plastics sheeting to protect them from the environment. For those grades which receive organic treatment at the final milling stage of manufacture, the carbon content is checked to confirm that the treatment has been correctly applied.

It will be evident that all this analytical testing is aimed at confirming that the processing has been carried out according to the laid down procedure. In most cases the results obtained from final packed pigment can be related to the processing conditions that have already been noted in the factory records. It is essential that such confirmation is obtained because properties like durability cannot be evaluated before the pigment is sold. Even testing in accelerated weathering equipment takes months rather than days, and the rarity of adverse comments on durability that have been ascribed to pigment failure offers ample justification of this approach.

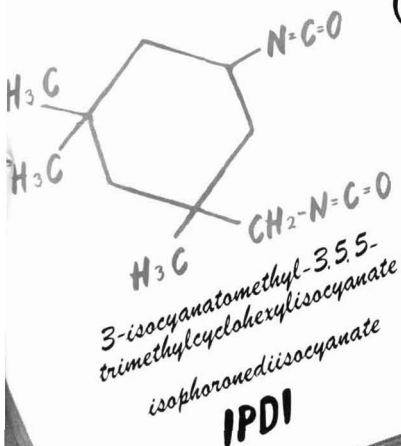
Physical properties can be much more directly associated with the practical performance expected of a pigment, and the most important ones will reflect dispersibility and optical properties. As has already been stressed, ease of dispersion has largely been ignored in the preparation of specifications for titanium dioxide pigments: and yet all other properties lose their importance if

a pigment cannot be dispersed in a customer's formulation and using his milling equipment. During the last 20 years or so paint makers have become more and more energy-conscious and immense demands have been made on pigment quality. The days when overnight ball milling was the norm have gone, with most paint manufacturers expecting to be able to disperse pigment in less than an hour.

Dispersion testing has always been important in the titanium pigment industry and as the quality of pigments has improved the testing and assessment has become more critical. One of the earliest tests used in the TiO<sub>2</sub> organisation consisted of milling pigment in alkyd resin solution using an automatic miller. The resulting paste was thinned with further resin and solvent and then poured out on to a glass slide. The state of dispersion was assessed in terms of the number of nibs apparent in the dried film and also by means of a fineness of grind gauge. The aim, of course, was to produce a nib free film and a "clean" gauge. At various times other means of dispersing pigment were used – ball mills, triple roll mills etc. – but these tests were carried out in the Technical Service Department rather than in the Control Laboratories. The next step was to resort to high speed stirrers as this type of milling equipment was being introduced into the paint industry, and a variety of stirrer blades were used on a laboratory scale. At the same time the preparation of the film in which over-size particles were being assessed was subjected to greater control, spinning tables ensuring both uniform and constant film thickness. At one time separate films of two thicknesses (3µm and 10µm) were prepared so that nibs of different sizes could be observed by observing the film surface.

Today, testing for dispersion in alkyd resin is carried out in a miniature high speed impeller mill with a small saw toothed impeller, and the assessment of dispersion is made solely by means of a fineness of grind gauge. This test has proved itself over many years of being capable of identifying pigment that will disperse satisfactorily on large scale equipment. In the early days this represented a minor proportion of pigment production, but as high speed dissolvers have become more common for paint making, resulting in an increased demand for this quality, pigment manufacturers have responded to the extent that most modern grades of titanium dioxide can be dispersed in this way. Improved dispersibility provides an excellent example of the effect of competition on pigment quality: pigment manufacturers, encouraged by their customers, have vied with each other to produce products which would disperse more easily.

Optical properties of pigments are greatly influenced by the state of dispersion of the pigment and ideally they should be examined in practical paint systems appropriate to the probable usage of the pigment. Nevertheless two basic tests have persisted in the belief that they will give some idea of consistency of quality of pigment. These are dry colour and lightening power (traditionally known as tinting strength). The colour of a pressed cake of pigment is compared with that of a standard pigment prepared at the same time. Any marked deviation from normality is indicative of a malfunction in the factory probably concerned with the chemical purity of the product. Specifically the inclusion of excessive amounts of elements having coloured oxides, e.g. iron and copper, will have a deleterious effect on the whiteness of the pigment. This may be reflected in the colour of a pigmented product and in cases of doubt the colour of a white paint is also assessed.



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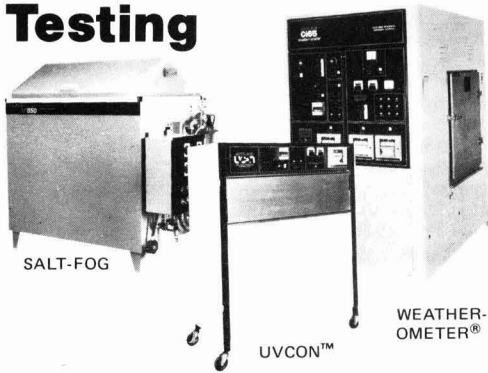
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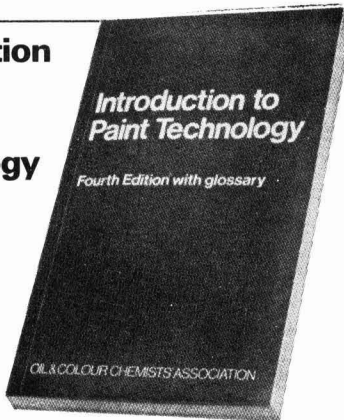
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Lightening power in terms of the reflectance of a tinted paste based on a selected medium indicates the scattering power of a pigment. The coloured pigment may be blue or black and the medium an oil or a solvent-free alkyd, and the rating of a pigment may be quoted as a percentage of the strength of a standard pigment or on a numerical scale relative to white lead having a value of 100. On this scale modern rutile pigments give values greater than 1800. Generally speaking lightening power is proportional to opacity, with the proviso that the state of dispersion of a pigment in a dry paint film will depend not only on the intensity of milling but also on the interaction between the pigment and resin. For this reason lightening power is often assessed in tinted paints, though the possibility of flocculation of the coloured pigment introduces yet another complication.

Associated with lightening power is undertone, a property that is seldom mentioned outside the pigment industry. Undertone is largely a function of particle size, which determines the ratio of scattering of red and blue light from the extremes of the visible spectrum. Thus, in general, pigments with a small particle size (so called fine crystal grades, primarily recommended for plastics) will have a blue undertone while larger particles will give rise to brown undertones. Careful control of undertone is essential for pigments used in coloured paints, especially those available from shop-based dispensing units where the colour is chosen and mixed at the point of sale. Another area of importance is in paints for automotive repair when accurate colour matching is vital.

Lightening power and undertone can both be assessed from colorimetric measurements but more usually visual comparisons are made by experienced operators who can detect very small differences. Dry colour is also compared visually, but on those occasions when paints are prepared for comparison of pigment colour, instrumental techniques are preferred.

The tests already described are carried out on most pigments, but there is another series which is derived from the applications for which specialist pigments are designed. Thus, pigments recommended for use in industrial stoving finishes, printing inks and water-based paints respectively are tested in appropriate systems. In industrial paints, gloss development and colour stability are considered to be critical as far as pigment choice is concerned. Paints are prepared in a conventional alkyd/melamine-formaldehyde system and stoved films examined for both colour and gloss. The latter is usually measured at an angle of 20° in order to increase sensitivity. Duplicate films are stoved at a higher than normal temperature and also for a longer time, causing loss of gloss by film shrinkage and also some yellowing. The overbake gloss test is particularly sensitive as an indicator of the state of pigment dispersion and only especially refined pigments will give high values.

The state of dispersion is also vital in glossy printing inks, where film thicknesses of only a few micrometres will show up even small variations in dispersion. It is perhaps not unfair to state that the ink industry is one of the most demanding of pigment quality. Nitrocellulose inks are prepared by high speed stirring and applied as duplex drawdowns so that sample and standard can be compared for gloss and opacity. Neither gloss nor opacity can be maximised with the same pigment since the particle size to give the highest opacity is too high for the best gloss.

Hence it is necessary to compromise to provide the quality required by a particular customer.

In aqueous paints, principally decorative emulsion paints, the important basic parameters are dispersant demand – the minimum amount of dispersant necessary to peptise a pigment slurry – and water demand in the presence of dispersant. Unless these properties are carefully controlled there may be difficulties in dispersion in sensitive systems. In addition, ease of dispersion may be tested and with heavily coated pigments such as Grade R3 of ISO/591, matt emulsion paints are made and examined for colour (whiteness), opacity, sheen and tint reduction. In all cases, the test pigment and a standard sample are compared either visually or instrumentally. Generally it is sufficient to make an overall visual assessment which will include both colour and opacity, since measurements are often confused by the surface texture of a low gloss latex paint. Finally reactivity in a simple emulsion paint is examined. This comprises the manufacture of a paint containing only pigment, dispersant, water and latex and observing its change in viscosity on storage at 40°C. The effect can be exaggerated by using less than the optimum dispersant concentration. As with water demand, any variation in reactivity can denote a change in the pigment coating.

To summarise, a pigment is characterised by testing that is appropriate to its final use. This means that not all pigment grades are subjected to the same range of tests, nor to the same level of performance.

## Conclusions

The specification of a raw material such as titanium dioxide that exists in a wide range of types, and is used in an even greater range of products, is a complex problem. ISO and other standardising organisations have attempted to identify those properties of a pigment that can be specified and are relevant to the final use of the pigment. It is considered that they have not been completely successful and indeed it is doubtful whether they can be. The solution to the problem really lies in the hands of the pigment suppliers and their customers, and in a highly competitive and technological industry, improvements in quality will be induced from both of these sources. On the one hand, pigment manufacturers will produce new products that are better than those of their competitors and will market these for particular applications; on the other hand, pigment users will demand higher quality from their suppliers as their own requirements become more exacting: continual striving for better whiteness, higher gloss and greater opacity together with improved durability and ease of dispersion has resulted in equally continual changes in titanium pigments. In turn this has led to more stringent control of quality by the pigment manufacturers. The pressure has come from customers not from standards committees, and the demands of industry have largely been met.

## Acknowledgement

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# Prediction of performance of exterior wood coatings

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## Summary

Although wood has been used as a building material since the dawn of time, the effective surface protection of wood components remains a source of considerable difficulty. This is partly a result of changes in wood and in the way in which it is used in modern buildings, and of a failure to take account in the formulation of coating systems of the requirements of wood as a substrate. The lack of accepted methods for predicting performance also hinders advance. This paper will review the factors underlying the performance of coatings on exterior wood and discuss methods of predicting the performance of natural and opaque wood finishes.

## Introduction

Surface coatings for exterior wood are a long-standing source of problems for the paint industry, and of dissatisfaction for users. Unsatisfactory finish performance may arise from a variety of causes in individual instances, but there are two general factors of major importance. The first is a failure very often to ensure in the design, construction and maintenance of wooden components that acceptable substrate condition is retained in service, by preventing the development of excessive moisture contents, or deterioration of the surface through exposure to weathering. The second is the production of surface coatings which are inadequate for the very exacting conditions often encountered on exterior timber.

The last few years have seen considerable development work in the paint industry aimed at producing wood coatings with improved durability. Moreover the problems of factory finishing of joinery components are now being addressed in collaboration with the joinery industry. This has generated interest in more relevant test methods. There is general recognition that conventional panel exposure tests, while they may yield useful information on coating durability, do not on their own provide a reliable guide to long-term performance on wooden components in service. A wide variety of test procedures have consequently been devised by different bodies with the objective of more closely simulating practical service conditions, though there is as yet no consensus on the performance criteria which are most relevant for wood finishes.

This paper will review the characteristics of wood as a substrate, and present experience at Princes Risborough Laboratory on the assessment of exterior wood coatings.

## Wood as a substrate for surface coatings

With the exception of a few difficult species, wood is regarded as providing a receptive surface for paint. The film formation and initial adhesion of most types of coating to a clean, sound wood surface rarely present difficulty. Moreover a substrate condition which would be considered suitable for painting is relatively easily

achieved, especially under factory conditions. Often however, notwithstanding the application of a good coating system, deterioration in the substrate is liable to occur during service, through the development of high moisture contents, photodegradation, or degradation by micro-organisms.

## High moisture content

High moisture contents are bad not only for the wood, they also have very serious consequences for the finish. For most wood species moisture-induced dimensional movement under service conditions is of the order of a few per cent, which though accommodated by most finishes when young, is a common cause of breakdown of aged embrittled coatings. High moisture contents in wood may reduce coating adhesion, and can lead to deterioration of the coating through hydrolysis or colonisation by staining fungi. In short the performance of the finish is strongly dependent on the wood substrate remaining dry in service.

Although the restriction of water entry into wood has been regarded traditionally as one of the most important functions of a surface finish, it is now generally recognised that a major cause of high moisture contents in present day fabricated joinery components is water which circumvents the coating by entering via unpainted surfaces in the joints. Since moisture permeability in the longitudinal direction may be two to three orders of magnitude higher than lateral permeability, the main route for moisture penetration will be through the end-grain.

The extent of wetting is strongly dependent on the permeability characteristics of the wood. For impermeable timbers, water penetration and its adverse effects on coatings will be restricted. The superior paint performance often found on timber components in older buildings is partly attributable to the use of impermeable and dimensionally stable heartwood of Baltic redwood and Douglas fir, which provide relatively inert substrates. The practice of sealing the end-grain by dipping joints in lead-based primer before assembly which has been common practice in the past must also have contributed.

By contrast in sapwood, and especially in pockets of overporous sapwood, the spread of moisture may be surprisingly rapid. This has been highlighted in simple tests at PRL<sup>1</sup> in which softwood sticks (150 mm × 38 mm × 38 mm) painted on their lateral faces with a three coat paint system were stood vertically with one transverse face in contact with wetted cotton wool. After an appropriate interval the moisture content was measured at successive one centimetre distances from the wetted end up to a height of 100 mm using an electrical resistance moisture meter. Typical results for Scots pine after 24 hours wetting are shown in Figure 1, including data for sapwood, heartwood, sapwood treated with water-repellent preservative by three minute immersion, and sapwood end-sealed by dip application of solvent-

<sup>1</sup>Paper presented at the Association's York Conference, 15-18 June 1983. An edited transcript of the discussion that followed this paper can be found on page 318.



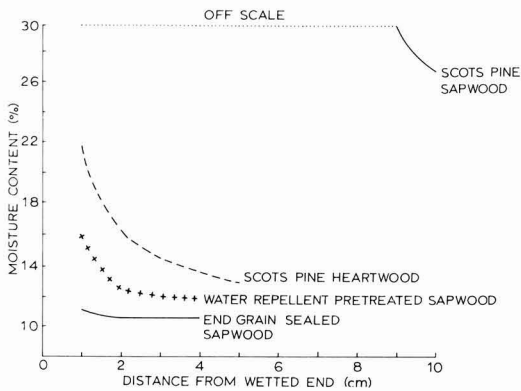


Figure 1. Water uptake into softwood sticks

thinned low-lead wood primer to BS 5358. It can be seen that Scots pine heartwood and sapwood show pronounced differences in behaviour; in heartwood, moisture contents were only moderately high and restricted to within 30 mm of the wetted end, whereas in sapwood moisture spread was extensive and exceeded fibre saturation point to a height of over 90 mm. The figure also shows that resistance to end-grain water entry into sapwood is increased by treatment with water-repellent preservative, and even more effectively by solvent-thinned wood primer. Tests on a wide range of different types of end-grain sealer have shown that varnishes, glues and pigmented coatings all provide some restriction to water entry, though effectiveness varies widely. Both binder type and level of pigmentation have an influence.

The effectiveness of end-grain sealers is being further assessed in long-term field trials using the L-joint specimens described by Carey<sup>2</sup>, each joint consisting of two arms measuring 203 mm x 38 mm x 38 mm joined by a bridle joint (Figure 2). The arrises of the horizontal member containing the tenon were rounded to a 3 mm radius to eliminate the risk of premature coating failure.

The joints were assembled without glue or pins. To produce sealed joints a low-lead solvent-thinned wood primer was applied by dipping the joint areas immediately before assembly; unwanted primer being wiped from the lateral faces. Unsealed L-joints were simply pushed together. Lateral surfaces were either unpainted, or painted with a three coat paint system and the assemblies were exposed outdoors at PRL for over 18 months. Figure 3 shows the results of measurements made using an AEI microwave moisture meter on the vertical arm of unpainted assemblies. The response of the unpainted specimens without a sealed joint is typical of that expected for bare wood in showing cyclic wetting and drying phases broadly corresponding to the seasons of the year; moisture contents were above 40 per cent (off-scale on the meter) for almost half of the exposure period. In comparison the unpainted/end-grain sealed L-joint showed consistently lower moisture contents, and off-scale readings were only obtained for relatively short periods. The underlying trend is nevertheless for moisture levels in the sealed joint in concerned with methods of restoring weathered wood to yield acceptable finish performance, and long-term weathering trials of ers are now being evaluated.

The results from painted L-joints are shown in Figure 4. The painted specimens without a sealed joint maintained very good control over moisture entry until the film cracked over the line of the joint after a few weeks of

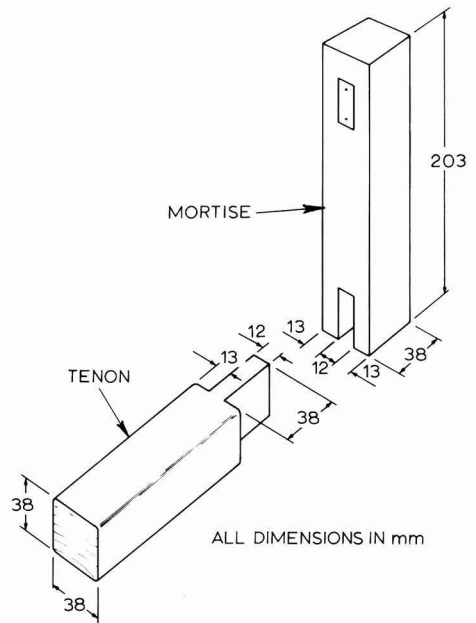


Figure 2. Dimensions of L-joint assemblies

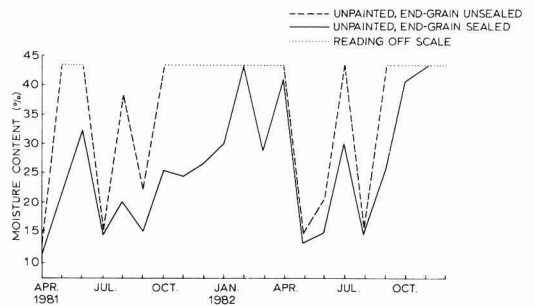


Figure 3. L-joint assemblies - water uptake into unpainted joints

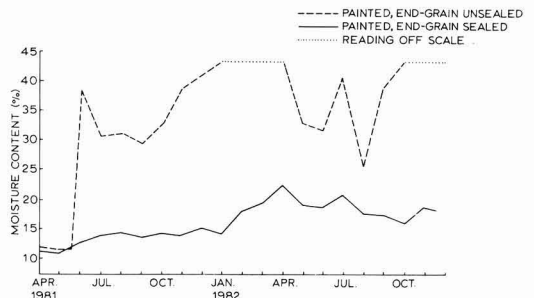


Figure 4. L-joint assemblies - water uptake into painted joints

exposure, allowing water to penetrate towards the hidden end-grain. A very sharp rise in moisture content ensued and moisture levels remained over 30 per cent throughout almost the whole of the exposure period. In comparison the painted specimens with a sealed joint exhibited very good control over moisture content, although again there is an underlying trend upwards. The differences in moisture levels in these painted assemblies were reflected





Figure 5. Comparison of paint performance on new (left) and weathered wood (right)

in paint performance, there being much more extensive film breakdown and fungal disruption of the paint on specimens with unsealed joints.

Comparison of the results for the unpainted/sealed and painted/unsealed assemblies in figures 3 and 4 yields a remarkable conclusion: that a small amount of wood primer applied to end-grain surfaces only has proved more effective in controlling wood moisture content over the period than application of a three-coat paint system over all of the visible lateral wood surfaces.

This work has confirmed that the predominant route for water entry is through end-grain. To permit entry of large amounts of water in this manner negates previous efforts to control wood moisture content during seasoning and component manufacture. Yet there has been a general tendency to regard water entry at joints as inevitable and to attempt to mitigate the consequences by impregnating with fungicides to prevent decay and by adopting more

permeable wood coatings to permit water to escape more readily.

Highly permeable coatings will facilitate the drying of wet wood, but risks of wood movement, surface splitting and mould disfigurement will be incurred. The objective should be to prevent the uptake of water in the first place. Very substantial improvements in coating performance on permeable timber would undoubtedly result if methods of preventing end-grain water entry which were effective, practicable and permanent could be introduced. The most promising approaches would seem to be end-sealing of joints before assembly and the use of improved pretreatments; these are currently the subject of further investigations at PRL.

#### Photodegradation

One of the most common causes of high maintenance costs for exterior painted woodwork is the presence of wood which has been subject to photodegradation during weathering. Weathered surfaces have been shown by Boxall<sup>3</sup> to cause premature breakdown of maintenance paint, as illustrated in Figure 5. Photodegradation has especial significance for natural finishes in that the most common cause of failure is breakdown of the substrate by light transmitted through the coating.

Part of the PRL finishes programme has been concerned with methods of restoring weathered wood to yield acceptable finish performance, and long-term weathering trials of alternative strategies are in progress. The overall result so far has been to establish the relative ineffectiveness of either resinous pretreatments or of mechanical methods of restoration. This would seem to be an area in which prevention is most definitely better than cure.

The first phase of an investigation at PRL into the mechanisms of photodegradation has also been reported<sup>4</sup>. The objective was to establish the relative effectiveness of the different wavelength regions in sunlight – information which is fundamental in the development of measures to prevent photodegradation. The criterion adopted for determining the degree of photodegradation during solar irradiation is the loss in tensile strength of wood strips about 150  $\mu\text{m}$  in thickness, in Scots pine and lime. The strips were exposed to measured doses of solar irradiation behind various filters and withdrawn at intervals for tensile testing.

This work showed that exposure of wood to sunlight results in a rapid reduction in its surface integrity. Table 1 shows typical results obtained for pine veneers exposed for five months during June-October behind a filter (G1) which transmits virtually the full solar spectrum, and a P4 filter which transmits only visible wavelengths.

Table 1  
Chemical and tensile strength changes in weathered Scots pine veneers

	Unexposed	G1 filter, cut-off 290 nm	P4 filter, cut-off 400 nm	Opaque filter
Tensile strength $\text{MN m}^{-2}$	59.94	9.80	17.0	55.2
Solubility in cold water (%)	1.6	26.6		
Solubility in hot water (%)	2.3	38.0		
% methoxyl	4.7	2.05		
Degree of polymerization of holocellulose	1300	470		

The results indicate that strips exposed behind a filter transmitting the full range of solar wavelengths suffer a marked loss in strength, and that this is attributable to a breakdown of the lignin, as reflected in the fall in methoxyl content, and to a pronounced degradation of the holo-cellulose to low molecular weight water-soluble products. From the standpoint of integrity and solubility characteristics, the weathered material cannot be considered to be wood any longer, and is totally unsuitable as a coating substrate.

Although as can be seen photodegradation is most severe in wood exposed to the full range of solar wavelengths, strips exposed only to visible light are also degraded. Subsequent work has indicated that visible light may account for half of the degradation occurring in Scots pine. This finding is of great practical importance because it imposes a limitation in principle on the performance of clear and semi-transparent finishes. It implies that the route to durable natural finishes lies in the use of pretreatments which stabilise the wood against photodegradation.

### **Degradation by micro-organisms**

During recent years the PRL research programme has included significant effort on microbiological interactions with surface coatings. A comprehensive review of the mechanisms of colonisation and strategies for protection has been given by Bravery and Miller<sup>5</sup>.

If wood becomes wetted it becomes susceptible to invasion by a range of micro-organisms which are also able to influence strongly the performance of the finish. Bacteria and microfungi cause increased permeability, which may result in problems from excessive uptake of solvent-borne preservatives during treatment or of water during service. Blue stain and mould fungi cause disfigurement and disruption of paints, and decay fungi bring about loss of adhesion and coating failure. The effects of all of these micro-organisms are generally more severe on permeable wood species.

From the standpoint of coating performance, the blue staining organisms pose the most serious and common problems, especially for varnishes and exterior wood stains, whose appearance can be irreversibly marred. The tendency for wood stains to possess higher permeabilities contributes to the problems, for they often permit the higher moisture contents at the surface of the timber which favour microbial development. The influence of coating permeability is also evident in results of BS 5082 type exposure tests<sup>6</sup> on wood primers using horizontal grooved panels in European redwood sapwood. Water-thinned primers usually demonstrate inferior mould resistance compared to solvent-thinned types when applied at a similar 25  $\mu\text{m}$  thickness, but can be equivalent when their thickness is doubled.

To be effective, protection against blue stain in service should aim to prevent colonisation of both the substrate and the surface coating. Experience and testing have shown that fungicides such as tri-*n*-butyltin oxide and copper/chrome/arsenic used in conventional preservative pretreatments against decay are often only temporarily effective against blue stain in service. Prevention of blue stain organisms requires fungicides specifically active against them. Work at PRL<sup>7,8</sup> and the Paint Research Association<sup>9</sup> has shown that certain sulphamides, sulphones, sulphonamides, thiophthalamides and carbamates are very effective in preventing colonisation. Such materials have been included in some recently

introduced preservative pretreatment formulations to provide combined effectiveness against decay and blue stain fungi.

The benefits which can result from the inclusion of fungicides in the coatings themselves have been shown in work at PRL and the Paint Research Association. For exterior wood stains, inclusion of fungicides is essential and is normal practice; it confers effective protection under normal conditions of use. Although fungicides are not widely used in conventional paints, evidence already suggests that their inclusion could improve coating performance here also.

### **Methods of assessment for wood coatings**

During the last ten years the range of coatings available for exterior wood has increased considerably. In opaque systems, traditional alkyd paints are still widely used, and the increasing availability of British Standard solvent-thinned and water-thinned primers constitutes an advance. Concern remains over the suitability of some general purpose gloss finishes and especially undercoats for the exacting conditions on exterior wood. There is growing interest in the so-called moisture regulating paints, which can offer a better balance of permeability and mechanical properties, albeit at the expense of some lowering of initial gloss. Developments in water-thinned gloss paints now raise expectations of wider use of these materials out of doors, where the intrinsic durability of the acrylic polymers could offer significant benefits. For factory finishing, alkyds, two-pack polyurethanes and water-borne acrylics are all candidate systems.

User interest also remains high in semi-transparent wood stains for outdoor applications, including joinery.

The level of activity in the wood finishing field coupled with the growing recognition of the need for improved durability has heightened interest in reliable test procedures. The essential need is for the establishment of performance criteria which can form the basis for predictive tests for long-term durability. The determination of changes in the mechanical properties of coatings during natural or artificial weathering by, for example, tensile testing, internal stress measurements or microindentation tests can provide useful information. Extensibility may be related directly to the ability of coatings to accommodate dimensional movement in wood. The technique of measurement of coating extensibility on soft aluminium has been used at PRL and is discussed below. It seems likely that the application of acoustic emission techniques to tensile measurements, which has been described by Strivens and Rawlings<sup>10</sup> and which is also to be presented at the Conference, provides a more sensitive means of detection of coating failure.

Measurements of coating properties provide useful pointers to performance, but ultimate reliance must be placed on trials on wood substrates, because of the pronounced influence wood exerts on film formation and performance. Moreover there is usually also a need to assess the combined effectiveness of coatings and wood pretreatments.

### **Extensibility measurements**

Changes in extensibility during artificial weathering to BS 3900 Part F3 has been determined by the method described by Whiteley<sup>11</sup>, using chromate etched soft aluminium at 20°C and an extension rate of 5 mm/min, equivalent to 10 per cent per minute. The testing machine

Table 2  
Extensibility of components of paint systems

	Extensibility (%)				
	Hours artificial weathering (BS 3900) F3, 1971				
	0	100	300	500	1000
BS 5358 solvent-thinned primer	>25	19	10	6	
Non-standard solvent-thinned primer	9	8	5	5	
BS 2521 lead-based primer	25	17	5	5	
Aluminium primer (leafing)	18	10	8	5	
BS 5082 water-thinned primer	>25				>25
Solvent-thinned undercoat 1	7	5	4		
Solvent-thinned undercoat 2	9	6	3		
Lead-based undercoat	5	4			
Alkyd gloss finish 1	>25				>25
Alkyd gloss finish 2	>25				>25

was a model 1026 Instron. The onset of cracking was determined at  $\times 20$  magnification. Determinations have been made on a range of coatings; typical results for various proprietary primers, undercoats and finishes are shown in Table 2. They show the wide disparity between different materials in both initial extensibility and the extent of change during weathering. Even after 1,000 hours of exposure, gloss finishes possess an extensibility of 25 per cent, well above the minimum level of performance of 8 per cent after 300 hours weathering suggested by Whiteley. All of the primers except the non-standard low-lead type possessed a good level of extensibility initially which reduced during exposure. After 300 hours, only the BS 5358, BS 5082 and leafing aluminium primers satisfied the minimum requirement. It was the undercoats, however, which were particularly poor, all failing to meet the requirement. Such products must undermine the performance of otherwise durable primers and finishes, and are to be deplored from a durability standpoint. Work is continuing to relate extensibility measurements to performance on wood panels of several species exposed to natural weathering at  $45^\circ$  facing south at PRL.

#### Wood test specimens

The traditional test specimen has been a flat panel in quarter sawn western red cedar, as required in BS 3900:Part F6:1976. Parana pine has also been favoured. Both of these species are fairly readily obtainable in consistent quality, but they are relatively impermeable and dimensionally stable and are no longer considered to adequately represent the more exacting conditions encountered in service with a permeable and less stable species such as the sapwood of European redwood or Scots pine, which have consequently become more generally used in testing. Care in selection of redwood is crucial to the achievement of reproducible and repeatable results. Suitable criteria are laid down in the tests for resistance to natural weathering for water-thinned and solvent-thinned wood primers to BS 5082<sup>6</sup> and BS 5358<sup>12</sup> respectively, which are currently under revision. They include the exclusion of defects, heartwood and over-porous sapwood, the aim being to obtain a substrate exclusively of sapwood of normal porosity, and of specified growth rate. Before use there will usually be a need to pretreat the panels with a preservative formulation which is representative or of specific interest.

#### Panel exposure tests

At PRL some weathering trials have been carried out

using vertical exposure, but most work has utilised  $45^\circ$  exposure to induce a degree of acceleration. For natural finishes, a system devised by the Centre Scientifique et Technique de la Construction, Belgium has been employed. It utilises panels from the sapwood of European redwood, with a planed finish, exposed at  $45^\circ$  facing south. The panels receive periodic inspection and are recoated with the original treatment nine months after the commencement of exposure in March.

The results of a trial on a range of proprietary systems has been reported by Boxall<sup>13</sup>. It demonstrated that current proprietary products vary widely in performance. After the first nine months exposure, many semi-transparent products exhibited pronounced changes in appearance through colour change, fungal disfigurement or incipient flaking, which could not be rectified by over-coating. Some semi-transparent stains performed much better, and panels finished in opaque coatings were virtually defect free and maintenance was deemed unnecessary.

It is considered that an eighteen month exposure period combined with adhesion measurements makes it possible to predict with some confidence the performance of systems during service conditions. The results of adhesion measurements on mid-brown stains and white paints are shown in Table 3. They illustrate the varying effectiveness of stains in protecting the substrate against photodegradation, and the consistently high standard reached by the opaque coatings.

The degree of acceleration obtained through  $45^\circ$  exposure enables meaningful results to be obtained for exterior wood stains in 18 months, and for alkyd paints in about three years. For higher durability polyurethane and acrylic coatings, of interest for long-life factory applied coatings, a further degree of acceleration is desirable, and a shallower exposure angle of  $15^\circ$  has been adopted for these systems. This stems from the work of Davis<sup>14</sup>, who found that the optimum angle of exposure for rapid degradation is the mean of the angle which maximises direct solar radiation and that which maximises the diffuse component of sunlight. It was suggested that for south-east England the optimum angle of  $15^\circ$  yielded a 30 per cent increase in the rate of degradation compared with  $45^\circ$  exposure. Sherwood<sup>15</sup> at the Paint Research Association also reports significant increases in chalking in paints exposed at shallow exposure angles.

The extent to which testing conditions should be made

Table 3  
Adhesion changes after 18 months exposure (after Boxall<sup>13</sup>)

	Unweathered coating		Weathered coating	
	MPa	S/D*	MPa	S/D*
Stains: one-can types				
S1	17.0	1.8	14.6	0.2
S2	14.9	0.4	10.4	1.4
S3	15.8	2.7	10.3	2.4
S4	11.0	1.8	8.5	1.8
S5	7.7	1.7	6.3	0.7
S6	17.9	3.3	7.8	2.2
S7	16.8	3.0	12.5	0.6
S8	9.0	0.6	9.1	1.7
S9	9.8	2.5	10.0	1.0
S10	3.2	0.6	3.0	2.7
S11	6.6	1.0	6.5	0.8
Stains: system types				
S12	16.4	0.0	7.9	1.3
S13	12.2	0.7	9.0	1.3
S14	17.3	2.5	14.6	3.1
S15	13.6	2.5	10.4	1.1
S16	16.2	0.6	11.5	1.3
S17	9.2	1.2	9.4	1.5
Mean	12.6		9.5	
Paints: one-can types				
P1	9.8	0.7	9.6	0.8
P2	13.5	0.7	12.7	0.6
P3	13.3	2.6	11.8	1.5
P4	12.3	2.1	13.1	2.9
P5	14.7	1.1	12.3	2.3
Paints: system types				
P6	15.5	0.6	16.2	0.3
P7	16.7	1.9	18.4	0.2
P8	15.5	0.6	13.3	3.1
P9	13.9	1.8	15.8	0.7
P10	17.8	2.8	17.1	1.1
Mean	14.3		14.0	

\*Standard deviation

more severe by the introduction of sharp edges or grooves in the panels has been the subject of much debate. The horizontal test panel with a groove devised by the Paint Research Association<sup>16</sup> has been widely used and earlier formed the basis of BS 5082 for water-thinned primers. The practical difficulties of ensuring a clean machined finish in the groove and thereby a continuous paint film, coupled with the amount of water collection in the groove make this a very severe test indeed. Experience suggests that the harshness of the test can distort results, especially by generating excessive mould growth, and it is now concluded that the effects of water entry are more meaningfully reproduced using jointed components.

#### Window frame trials

Extensive trials have been carried out on test windows in a window joinery test building (Figure 6), designed to allow exposure of test windows in simulated severe service conditions through the control of internal temperature and relative humidity. Moisture contents at various positions around the frames have been monitored using either probes or a microwave moisture meter. The results of comparisons of exterior wood stains and paints have been reported<sup>17</sup>.

Window frames are in many respects ideal test

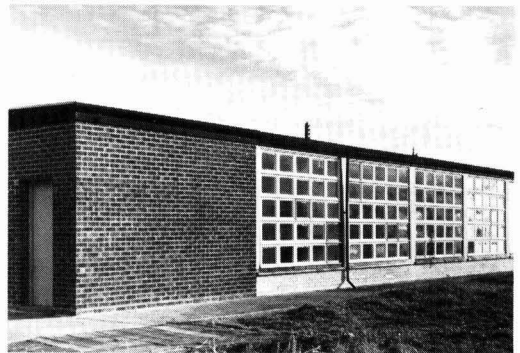


Figure 6. Joinery test building

specimens in that they directly reproduce conditions in service and allow the influence of jointing and glazing to be assessed. It was the trials at PRL which emphasised the profound influence of end-grain water penetration on coating performance. The disadvantages of using test windows are that they are relatively expensive to prepare and that it is difficult to ensure that similar timber is present in different frames. In particular it is rarely possible to exclude heartwood entirely, and the best that

Table 4  
Effect of coatings on strength loss in thin strips exposed to sunlight

	Tensile strength (arbitrary units)			
	Unexposed	8 weeks	20 weeks	32 weeks
Untreated pine	6.97	5.74	3.92	3.35
Alkyd varnish	9.34	7.47	6.81	6.04
Alkyd + UV absorber	9.37	8.79	8.04	7.38
Low build				
Exterior wood stain (1)	9.48	7.97	7.60	6.15
Exterior wood stain (2)	9.50	7.32	6.72	6.05
Solvent-thinned primer	10.33	9.39	9.62	9.19

can usually be done is to restrict it to the interior face of the sections and to the top rail, which is usually of less interest. Experience at PRL has shown that performance around the bottom joints can be simulated using L-joint specimens, which have a number of important attractions. L-joints are consequently used to an increasing extent in coating evaluation, and window frame testing reserved for long-term testing of systems of especial interest.

#### L-joint testing

The L-joints described earlier have been found to provide an extremely reliable and reproducible means of simulating the performance of coatings and pretreatments on jointed components. The relatively compact cross-section of 38 mm × 38 mm provides horizontal and vertical surfaces of size sufficiently adequate for coating assessment, and yet is small enough to permit selection of a consistent quality of timber. Reproducibility in terms of moisture response and coating performance has been found to be unusually high, so that the use of duplicate specimens is sufficient. Moreover the severity of substrate wetting can be varied by, for example, the presence or absence of endsealer, or by cutting the paint over the line of the joint before exposure. If the paint film is left intact, the period of time before it cracks during exposure serves as a useful indicator of extensibility.

The value of the L-joint test may be further enhanced by subjecting specimens to microbiological assay at intervals during exposure, as described below. The method then enables a comprehensive evaluation to be made of the durability of pretreatment/coating systems and their effectiveness in controlling wood moisture content and microbiological attack.

#### Tensile measurements on thin wood strips

The technique for assessing tensile strength changes in thin wood strips referred to earlier was originally developed at Princes Risborough as a predictive test for the performance of preservatives in ground contact situations. It has been found to offer promise for predicting the effectiveness of pretreatments and coatings in preventing deterioration of wood through photodegradation. The technique has the advantage that large numbers of test specimens can be prepared by microtoming a relatively small block of wood, which minimises the influence of wood variability.

In a current trial a range of coatings and pretreatments has been applied to pine strips and exposed to the full solar spectrum under filters. The treatments were applied as one dip application followed by one brush coat to the irradiated face. Table 4 shows the results obtained after 32 weeks exposure for the following systems: long oil alkyd

varnish, with and without the addition of ultraviolet absorber of the benzophenone type; penetrating exterior wood stains; solvent-thinned wood primer. Tensile strengths were measured in this instance using a Pulmac short span testing apparatus at a jaw separation of 1.6 mm.

Comparison of the results for treated strips compared with untreated shows that all of the treatments have an initial reinforcing effect. Strength loss occurs during irradiation, but is retarded by the coatings to varying extents. The influence of the ultraviolet absorber in retarding breakdown under the alkyd film is evident, as is the influence of pigmentation with the relatively opaque wood primer providing most protection. The application of this test method to the assessment of coating systems is relatively new, but it shows promise for the determination of the extent of interaction of polymers with wood, and of the effectiveness of protection during weathering.

#### Resistance of coatings to fungal attack

Considerable progress has been made in recent years, much of it at PRL, in the development of reliable and reproducible methods of test for coating resistance to fungi causing mould, blue stain in service, and decay.

#### Mould growth

The spores of mould fungi are present in large numbers in the air at most times and there is a constant risk of mould growth whenever surfaces become wet. However during outdoor exposure, conditions are constantly changing which means that reproducible testing is difficult. Tests have therefore been developed which can be conducted under constant and controlled laboratory conditions (Bravery *et al.*<sup>7,18</sup>).

The principle of the methods is to inoculate paint films applied to either glass tubes or panels of wood, plaster, metal etc. with a specified mixture of mould spores and incubate under conditions which promote high condensation (Figure 7). After four weeks, susceptible control paints show severe mould growth. The resistance of particular coatings or of fungicides added to the paints is assessed using a subjective rating scale of 0 for no mould growth to 5 when more than 70 per cent of the surface is affected. Results have been shown to be consistent and repeatable<sup>19</sup>. The methods are equally applicable to primers, undercoats and top coats and can be adapted for masonry coatings also.

#### Blue stain in service

Methods have been developed for testing the resistance of natural finishes and of pretreatments which enable the pre-



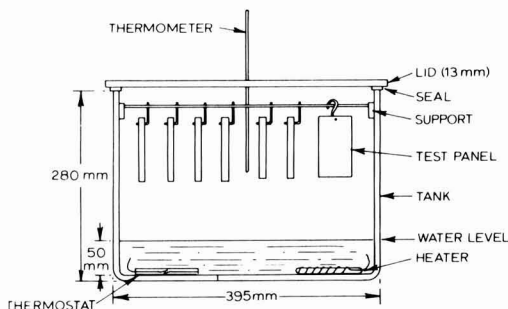


Figure 7. Mould growth test cabinet

ventive product to be applied by brush (Butin<sup>20</sup>) or by an industrial process<sup>8</sup>. After pretreatment by the desired process, the test coatings are applied and subjected to natural or artificial weathering. Natural, BS 3900 Part F3 and certain artificial weathering machines have been shown to give closely comparable results. Panels are then inoculated with fungi under controlled laboratory conditions and after six weeks incubation the extent of blue-black disfigurement is assessed. In addition the mean depth from the surface of the stain free zone is determined.

#### Decay fungi

Ecological studies have revealed that a sequence of fungi are involved in the eventual decay of softwood window joinery<sup>21,22</sup> and that an interrelationship exists between them, which is in turn influenced by the varying natural weather conditions. For these reasons the L-joint technique previously established by Banks<sup>23</sup> and Purslow and Williams<sup>24</sup> has been adapted by Carey<sup>2,22</sup> to provide a more realistic model test for joinery fungicides.

L-joint assemblies treated by appropriate processes with preservatives are exposed on racks and three replicates are harvested at particular intervals of time such as 6, 12, 18, 24 and 48 months. At each harvest the lower part of the joint assembly (tenon) is dis-assembled and dissected to yield a set of samples for moisture content and porosity assessment and a sample from which isolations are taken (Figure 8). Using selective microbiological growth media the presence or absence of blue-staining, soft rot and decay inducing *Basidiomycete* fungi can be determined. The extent of change in porosity along the tenon member gives an overall indication of the progressive extension of microbial activity away from the joint. A comparison of the rates of development of the different organisms can give a comparative indication of the relative efficacy of different treatments (Table 5).

Table 5

Colonisation sequence of organisms isolated from L-joints (after Carey<sup>23</sup>)

Type of organism and feature	Time of first isolation (days)		
	Untreated	1% TnBTO	5% PCP
Bacteria	11	11	11
Blue stain	11	11	32
Soft rot	11	43	375
Blue stain pustules erupting	32	130	375
<i>Sistotrema brinkmannii</i>	43	221	2 years
White rot fungus	32	375	
Visible white rot	4 years		
Visible brown rot	5 years		

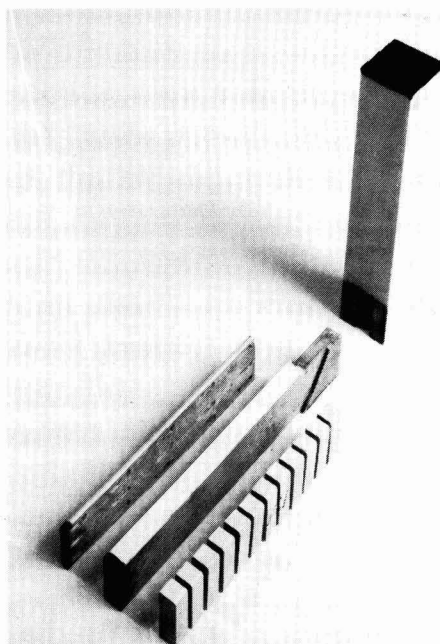


Figure 8. Conversion of L-joint assembly for microbiological assay

#### Conclusions

Exterior wood is an exacting substrate for surface coatings, but evidence suggests that the difficulties could be solved by measures to prevent substrate deterioration in service through high moisture content, photodegradation or biodeterioration, and by the introduction of improved types of coatings. Efforts are being made to improve the design and construction of wood components, and there is increasing availability of coatings formulated for exterior wood. It is necessary that the comparative advantages of newer types of coatings be established, and test methods are available which permit the prediction of physical, chemical and biological aspects of deterioration with some reliability. L-joint tests would seem to offer particular advantages in that they enable a comprehensive assessment to be made of the durability of pretreatment/coating systems and their effectiveness in controlling wood moisture content and microbiological attack.

#### Acknowledgements

The author acknowledges helpful discussions with several colleagues, and in particular the contribution on microbiological interactions from Dr A. F. Bravery.

[Received 3 May 1983]

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## conference discussion

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Discussion is encouraged at OCCA Conferences following the presentation of papers. Those who put questions were asked to fill in discussion slips with the details of their questions. The answers given by the lecturers/authors were recorded on tape. Edited versions of the discussions that followed the papers published in this issue appear below: questions in ordinary roman type, answers in italic. Only those questions for which discussion slips were received are published.

### NMR analysis of paint media

#### M. Marshall

K. BORER: Why is the proton NMR technique not suitable for nitrocellulose? Is it just that nitrocellulose is not interesting enough or because semi-natural products are too complex?

*M. MARSHALL: The reason the technique is not suitable is partly because it does not measure the sort of things that are interesting in nitrocellulose. Also there are a number of practical problems: high molecular weight grades of nitrocellulose are not soluble in the sort of solvents that are used in proton NMR, deuteriochloroform for instance (although deuterioacetone can be used). We have looked, for example, at explosive grades of nitrocellulose and the results tend not to give answers which are of practical use. They will tell you that it's nitrocellulose but not the molecular weight distribution. If the nitrocellulose is highly nitrated there is a lack of protons anyway. The solubilities are also rather low for carbon 13 NMR unless a gel can be made, which is rather difficult.*

J. R. KELSEY: Are computers used for analysing NMR spectra as they are for infrared spectra?

*M. MARSHALL: Computers aren't really used for interpretation of spectra, although work has certainly been*

*done on interpretive programs. In principle, for small molecules interpretation of NMR spectra should be easier compared with IR spectra because there are quite well-defined rules. For large molecules you are back to a library matching type system.*

*However, computers are used a great deal in carbon 13 and proton NMR. They enable the Fourier transform technique to be used which gives an enormous boost in sensitivity. It is this technique that has made carbon 13 NMR a practical method rather than an academic curiosity. In this situation the computer is an integral part of the instrument without which the instrument could not work.*

R. B. TENNANT: Is there any possibility in the near future of speeding up the NMR process?

*M. MARSHALL: Yes, I think so. The time limit of the technique is essentially dependent upon sensitivity. The sensitivity of NMRs has doubled or quadrupled in the last four years for example. The square root relationship that exists means that quadrupling the sensitivity halves the time of the experiment; this is due basically to progress in electronics.*

### Efficiency and change in metal decoration

#### A. A. Gamble

D. A. KALWIG: With reference to white base coat for DWI cans, is pre-coated or coil coated stock used for can fabrication? And are water-based coatings used in the UK?

*A. A. GAMBLE: No, the white base coat for DWI cans is applied from a coating unit. This unit is similar to a print-*

*ing machine and applies the coating in the round. Water-based coatings are not used in the UK. In Europe a small amount is used, while in the States this type of coating is used a great deal - largely because of environmental pressures.*

J. R. TAYLOR: In distort printing do you regulate the type

of pigments and the PVCs used in the various coloured inks to control the gloss?

*A. A. GAMBLE: We don't because there is such a pronounced drop off in gloss due to the extrusion process. No matter how our own processes of ink manufacture are controlled this can in no way compensate for this enormous drop off.*

**B. F. GILLIAM:** The advantages of two-piece deep drawn cans for beverages are readily apparent. But I wonder why the paint industry has not adopted these containers, particularly for emulsion paints.

*A. A. GAMBLE: The problem is that these types of containers would have a very limited outlet in the paint industry because they can't be produced to accommodate large volumes. The greatest volume it is possible to cater for with the DWI process is around 2.5 kg. That's fine for the printing ink industry where 2.5-3 kg is the norm, but not for the paint industry.*

*However, in the paint industry, particularly on the emulsion side, we are seeing metal containers being replaced by plastic ones. Although the quality of design on the plastic containers is inferior - there isn't a high gloss and there is not a lot of screen work - it is not that important, I think cost is far more critical.*

**R. H. E. MUNN:** The major preoccupation of can makers appears to be that of cost reduction. The wider use of polyester resins in base coat whites for two-piece cans has enabled significant reductions in stoving temperatures with consequent economies. You have not made any reference in your talk to interior can coatings but would you comment on the use of electrodeposition as a more economical and efficient application method for such interior coatings?

*A. A. GAMBLE: To decorate cans already in the form of a container one has to achieve deposition rates commensurate with the line speeds of these containers. This involves speeds of up to 800 cans a minute, and although it is possible to split lines to some extent, I don't know whether electrodeposition could cope. But that's only what's being achieved now, already printers are talking of pushing these speeds up to a 1,000 cans a minute; however the spray techniques of the sanitary coatings are beginning to cause problems.*

**R. H. E. MUNN:** Coming back on that, I think electrodeposition is a possibility in that when you are trying to coat the interior of a two-piece can you want virtually no throwing power, all you want is the ability to build-up film thickness in a very short time. Usually these things go hand-in-hand, so if you don't want good throwing power, which is the case, you should be able to get your speed of film build-up in these extremely short times. It might also be possible to overcome the current problems of porosity of spray coatings using electrodeposition. I think the difficult thing, however, would be sorting out the engineering side.

*A. A. GAMBLE: One of the problems of the two-piece can is that the sanitary coating is applied after the decoration stage. Consequently, if small droplets of coating or ink contaminate the interior of the can prior to spray coating, de-wetting may occur leaving exposed areas of metal. De-wetting will depend upon the nature of the lubricants present in the contaminant droplets and several cases of leaking containers have been put down to incomplete sanitary protection. If electrodeposition could help in completely wetting the inside of the can, that would be another reason for examining electrodeposition as an alternative means of applying these coatings.*

## Quality control and standardisation in the titanium pigment industry

**R. R. Blakey**

**R. L. J. MORRIS:** Your remarks indicate that international standardisation has not been successful in defining the types of titanium dioxide pigments in current use for paints. Can you indicate what role, if any, you see for the international standardisation of such products?

*R. R. BLAKEY: I'm sure there is a place for international standards, as well as British standards, for finished products, particularly consumer products; consumers otherwise would have little protection. In sophisticated industries such as the paint industry, however, the cooperation that exists between raw material suppliers and users is close enough to obviate the need for international or British standards.*

**D. S. NEWTON:** Firstly, do you consider that R3, described as rutile titanium dioxide but containing 20 per cent surface coating treatment, complies with the Trades Description Act?

And secondly, when a specification calls for a minimum amount of extender in the pigment phase, should the surface treatment in R3 be considered as part of the opacifying white pigment or as part of the extender?

*R. R. BLAKEY: I would say that R3 type pigments are titanium dioxide pigments, not titanium dioxide chemically. What we as titanium dioxide pigment manufacturers produce is mainly opacity and whiteness. In some circumstances that can be done more effectively by putting relatively large amounts of silica and alumina onto the surface of the titanium dioxide. So, provided that we refer to titanium dioxide pigment and not titanium dioxide as a chemical, I have no worries regarding the Trades Description Act.*

*Regarding your second question, I would say emphatically that the silica and alumina on the titanium dioxide is not part of the extender. This can produce*

*difficulties with analysis when a paint specification calls for paint to contain a certain amount of titanium dioxide. With an R2 type pigment which is, say, 93 per cent titanium dioxide, the assay comes out low. We as manufacturers then have to explain to the analysts the reason for the discrepancy, and why titanium pigments are not 100 per cent TiO<sub>2</sub>.*

**R. J. MCCAUSLAND:** In your paper you refer to undertone, linked to crystal size, as a property not often raised by the paint industry. With the increasing use of dispenser systems, both in production and in the retail trade, do you forecast an increasing awareness of this property and, if so, what specification would you suggest?

*R. R. BLAKEY: Undertone is a property examined by us regularly at the same time as lightening power, so we are well aware of its effect. As far as the paint industry is concerned there are certain very critical applications, in particular automotive refinishing, where undertone is vital. I agree with you that it is important for colour dispensing systems but our normal quality control will easily cope with the requirements for decorative paints.*

**K. F. BAXTER:** If you do not believe that British standards or international standards for pigments, especially

titanium dioxide pigments, have any use in industry, what proposals do you have for setting specifications which are meaningful for users of such pigments?

*R. R. BLAKEY: As I have pointed out, we already have our own fairly stringent specifications for a lot of different grades of pigment. I think the problem arises in trying to produce a general standard for titanium dioxide. We have in our range about half a dozen R2 pigments. For each one of these we have a different specification – each one is slightly different from the next one – although they all come into the same category in the British standard.*

*Generally speaking, we operate against what we call standard samples of pigments, so most of our testing is comparative. These standard samples for every pigment grade represent current average quality and are changed regularly. Over the years pigments have improved considerably, so that current sample stocks are much superior to those that existed 20 years ago.*

*So, we have a moving scale to specify against and we are always willing to discuss our specifications with any customer. This is the way in which specifications work between raw material suppliers and their customers, but because customers' requirements vary it is impossible to include every facet in a general specification.*

## Prediction of performance of exterior wood coatings

**E. R. Miller**

**E. L. FRENCH:** Would you care to comment on the role of what are referred to as microporous finishes for timber? You have explained that a lot of the problems, particularly to do with rot, are associated with the moisture content of the timber. But also there is the role that moisture plays in causing flaking of the paint film due to the water vapour pressure that can be generated beneath the film, and the degradation that takes place at that interface. It appears that within the last three to five years there has been a move towards applying thinner coats of paint which can breathe and which allows the timber to breathe.

I would also like to ask whether it is valid to show the results of accelerated weathering tests on undercoat when in fact one should really be evaluating the total system.

*E. R. MILLER: There is tremendous interest in microporous paints, though I must say I do not like the term as I do not think it has any scientific meaning. As you indicate, high moisture contents are bad for the wood and for the paint, and there is therefore a role for more permeable paint systems which will allow water to escape. On impermeable timber one is better off with an impermeable paint which will limit water entry into the lateral surfaces which are then the more significant route for water entry. For permeable softwood, however, paints possessing a higher degree of permeability than that of conventional gloss paints are desirable.*

*On the question of accelerated weathering tests, I*

*accept your objection that we were weathering the undercoat alone, and one must question the extent to which artificial weathering reproduces the changes occurring during the ageing of an undercoat protected by a gloss finish. It is useful however to look at the components of a gloss paint separately. The important point is not so much the magnitude of the rate of loss of extensibility during weathering, but that the undercoat possessed only 6 to 7 per cent extensibility initially. In the complete programme we are looking at the extensibility of full systems.*

**R. R. BLAKEY:** I would like to draw your attention to the work done in our company by L. A. Simpson on the mechanical properties of weathered paint films. Instead of testing elasticity by extension to breaking, we have tested by repeated flexing of films without going to complete break, which we believe reflects more accurately what actually happens in practice: as wood expands and contracts there is flexing of the paint film. We have come to the same conclusion as you that the undercoat is the most critical part of the system.

*E. R. MILLER: I am not suggesting that the extensibility technique we use is the ultimate, and I should be interested to hear more about your flexing test. The acoustic emission technique which Mr Strivens will describe later is another possibility for exploring at an earlier stage the changes occurring in the film.*

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## conference discussion

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### Linear polymonosulphide and polysulphide polymers – general survey, recent developments and applications\*

J. Brossas and J. M. Catala

J. R. TAYLOR: With regard to dicarbanionic polystyrene, it is stated that the solubility parameter will be increased by the presence of sulphur. Also, high gloss, higher transition temperature and good flexibility due to ease of rotation of the polysulphide linkage will be obtained. Have you any data on these physical properties and what will be the weathering characteristics of this new polymer?

J. BROSSAS: Actually, our work concerns the synthesis of new polymer polysulphides and we have no results on the physical properties or weathering characteristics of these polymers.

\*Paper published in last month's issue

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## next month's issue

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The Honorary Editor has accepted the following papers for publication in the November issue:

**Mechanistic model for corrosion protection via paint\*** by F. L. Floyd, R. G. Groseclose and C. M. Frey

**Acoustic emission – further unpublished results of the new technique for the study of paint performance during environmental exposure tests\*** by T. A. Strivens and M. S. Bahra

**Wood protection – the interaction between substrate and product and the influence on durability\*** by Å. Underhaug, T. J. Lund and K. Kleive

**Quality Control of coating application\*** by D. A. Bayliss

**Assessment of paints for the exterior bodysides of railway rolling stock (short communication)** by D. M. Bishop and D. Bottomley

\*Paper presented at the OCCA Conference, York, 15-18 June 1983. The relevant discussions that took place will also be published in this issue.

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## corrigendum

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The 23rd and 24th lines (left hand column) on page 135 of this year's May issue (*JOCCA*, 1983, 66(5), 132) are incorrect. They should have read as follows:

As it is known, lac contains about 70 per cent hard resin and 30 per cent soft resin<sup>23</sup>. Hard resin is a mixture of aliphatic and terpenic acids<sup>24</sup> whereas soft resin...

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## letters

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### Alternative driers

Re. June 1983 issue, page 155 – "Alternative driers to cobalt and lead"

Sir – as a paint-drier manufacturer I would like to comment that during the years 1954 to 1958 much work was carried out by various groups, and the writer, to find replacements for lead and cobalt.

It was established (as reported in my lecture to the South African Section of OCCA, 1961) that cerium replaces lead if used as detailed in my notes of that day, and that zirconium finds use in stoving enamels.

Further to this, I gave a short talk again to OCCA members on 26 July 1979 (reported in *JOCCA*, 62(11), 446, 1979).

It is disappointing to note that after many years of

trying to interest paint technologists in new drier/metal combinations, very few are prepared to evaluate or change from established combinations.

The only true success that I have had in this regard was to persuade the South African paint industry to change (for the better) naphthenates for driers based on synthetic acids. Curwen had the same problem in getting the industry to change from tallates and rosates to naphthenates.

However, I am pleased to report that one company here in South Africa is using our cerium naphthenates as a replacement for lead in a toy enamel, and that two companies are using our replacement for cobalt.

*Chelac Chemicals*  
PO Box 534  
Alberton 1450  
South Africa

*Yours faithfully*  
C. R. Chessman  
Managing Director  
12 August 1983

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## reviews

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### The Elements of Polymer Science and Engineering

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**A. Rudin**  
Academic Press  
New York, London, 1982  
pp. XV + 485

A science which generates 300 symbols in its first half century must be considered a major discipline, and a useful appendix to this publication lists these symbols. This publication is intended as a basis for a lecture course but can easily be used as an introductory text for newcomers to the polymer field. It deals essentially with the theoretical aspects of polymerisation: polymer molecular weights; polymer isomerism; step-growth, free radical, emulsion and ionic polymerisation; copolymerisation; polymer reaction engineering; mechanical properties of polymers; and polymer mixtures. It considers that the classical distinction between addition and condensation polymerisation is no longer valid since some polymers can be made by either route. Polymerisations as covered by the Carothers equation are now called step-growth polymerisations. Individual polymers and their properties are described only to a very limited extent but other books cover this field adequately. Most chapters conclude with a set of problems but to obtain the answers one must acquire a "Solutions Manual". There is an adequate

subject index and selected, but not comprehensive, references.

*Reader Enquiry Service No. 21*

*L. A. O'Neill*

### Developments in Polymerisation - 3

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**R. N. Haward, editor**  
Applied Science Publishers Ltd,  
London, New Jersey, 1982  
pp. xi + 243, £29

This volume is concerned with crosslinking and cyclisation in polymerisation reactions and contains five papers by experts in their fields. Cyclopolymerisation may be carried out as a deliberate process using divinyl compounds, or may occur as a side reaction in condensation polymerisation. The first paper (by Corfield and Butler) deals with the former case, and the third (by Stepto) with the latter. This is the most relevant paper for the coatings industry, as it is fundamental to the understanding of alkyd resin formation. A fourth paper (by Dušek) stresses the importance of cyclisation in free radical (co)polymerisation. The other papers deal with elastomer vulcanisation (by Morton) and photochemical crosslinking (by Ledwith). In the last-named, there is a brief mention of practical applications, viz. the use of photo-resists and radiation-curable surface coatings.

*Reader Enquiry Service No. 22*

*L. A. O'Neill*

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## occa meetings

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### Natal Section

#### Wood stains for the furniture industry

On Thursday 18 August 1983 at the Westville Hotel, Mr Tom Bebbington of ICI (UK) Ltd gave a most interesting lecture with slides on "Wood stains for the furniture industry". In it he outlined the reasons for staining wood, types of stains currently available and methods of application.

The types of wood stains available were divided into dyes and pigments (aqueous and non-aqueous) and chemical stains. The furniture industry tended to favour solvent-based dye stains over aqueous stains, which cause

grain lifting and a cloudy effect. With the advent of polyester and acid cured overlacquer systems there was a demand for better stains with improved solubility, miscibility and light fastness.

Mr Bebbington pointed out that unlike pigments it was not easy to state absolute values for light fastness on dyes due to the effect of the individual substrates. He recommended that users carry out their own tests in the relevant environment.

A short question time ensued followed by the vote of thanks from Mr Roly Eglington, who also thanked ICI for sponsoring the evening.

*R. Philbrick*

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## news

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### Anti-corrosion association

September saw the launch of a new trade association which will be of importance to companies in the sphere of corrosion control and painting inspection.

The new organisation is the Association of Anti-Corrosion Inspectorates, known as AACI for short.

Membership is open to any company or individual able to demonstrate a professional involvement in inspection of anti-corrosion methods and materials.

Among its main objectives, the AACI lists the establishment of a code of practice for inspection companies, the general improvement of industry standards, the training and certification of

inspectors, publicity and information about members and their services, the provision of industry input into such organisations as BSI, ICorrST and NACE, the representation of the views of the industry to all types of clients, and acting as an organising authority representing and promoting the interests of the anti-corrosion inspection industry.

*Reader Enquiry Service No. 31*



**The future of industrial coatings**

The market for industrial coatings, together with specialised types of coatings, is estimated to total over 6 million tons at present, approximately half the total world demand for all types of paint. It is anticipated that this will grow to almost 7.2 million tons by 1990, and will approach 10 million tons by the end of the century. This is one of the conclusions reached in the latest multi-client study of the coatings industry issued by Information Research.

The report predicts that throughout the rest of the present decade the trend away from conventional low-solids solvent-based paints towards high-solids and water-borne systems will continue. However, during the 1990s, both powder coatings and radiation-cured systems will make a significant impact on the market and together will account for over 20 per cent of the demand by the end of the century. The relative importance of all the various types of alternative coatings technologies up to the year 2000 are quantified in this study for western Europe, North America and Japan. Also, the likely dates by which each technology will achieve measurable market shares are predicted.

A general overview of the present state of development of each type of coating system and of application methods is provided, and the likely future developments are indicated. The factors that will affect the future of the industry are evaluated and placed in perspective. An analysis is also given of the acceptance rates of the newer coatings technologies by the main user industries, together with the forecast demands of each industry by type of coating system. In this context, western Europe, North America and Japan are treated separately.

Some guidelines are given for the evaluation of an appropriate strategic plan that will enable a company in the industry to exploit the opportunities that will exist in the future, and to ensure continued maximum profitability in the 21st century.

*Reader Enquiry Service No. 32*

**Opportunities in West Berlin**

West Berlin, whose population of two million equals that of Frankfurt, Dusseldorf and Hanover put together, is the largest industrial centre between Paris and Moscow. Besides its broad industrial infrastructure, skilled workforce and over 180 research and development institutes, it offers firms interested in expanding into West Germany and other European markets an exceptional package of tax free setting-up grants, low interest loans and a unique turnover bonus of up to 14.2 per cent of invoice value. Through

this package, it is claimed manufacturers in Berlin can obtain a higher cash flow and a higher return on investment than anywhere else in Europe.

The Berlin Economic Development Corporation (BEDC), an independent consultancy operating under the auspices of the Berlin government, provides a free and strictly confidential advisory service on what is available and it has recently appointed a representative in the UK, Mr John McKibbin at 31 Northway, London NW11 6PB, who can be contacted for further details.

*Reader Enquiry Service No. 33*

**Offshore installation protection**

At a recent one-day symposium in London the joint DOE/PRA report on "Survey of painting practice for protection of offshore oil installation" was critically appraised by a number of speakers who dealt in turn with the viewpoints of the clients, fabricators, paint suppliers, painting contractors and inspectors.

The discussion periods indicated that in spite of the fact that this industry is now into its second decade there are still many problems to be solved; the hundred or so delegates who were present indicated that the various parties involved were more than interested in trying to solve them.

A copy of the report is available at £30 from the PRA.

*Reader Enquiry Service No. 34*

**Chemical hazard evaluation**

Columbia Scientific Industries has recently introduced a commercial sample service. This enables chemical process engineers, chemists, safety specialists and researchers evaluating thermal hazards and their effects to obtain a data report on samples supplied.

The new service offered by CSI centres around the ARC which is used to simulate chemical processes, to study reactions in terms of time related to temperature and pressure, and to provide a data report on the hazards associated with processing, storage and, where applicable, transportation of the material tested.

Up to 20 grams of sample is tested inside a spherical bomb in a fully sealed system. The report can tell users of the service if there is a thermal hazard associated with the sample, and if one exists at what temperature it commences. It can also quantify the severity of the hazard and provide information on how it can be controlled. In addition, the service

gives data on the time limits available for any remedial action if control is lost, and if the processing equipment can be prevented from destruction in the event of total control loss. The service can also suggest means of storing the material and what precautions are needed for transportation. Samples can be submitted in solid, liquid or slurry forms and the equipment used for the test procedures can be demonstrated if necessary.

*Reader Enquiry Service No. 35*

**products**

**New TiO<sub>2</sub> Pigment**

Hombitan R 522 is a lattice-stabilised, coated and micronised rutile TiO<sub>2</sub> pigment.

According to Sachtleben, the manufacturer, special features of Hombitan R 522, which has a wide range of uses, are its easy wettability and very good dispersibility in all types of systems.

Enamels and printing inks pigmented with Hombitan R 522 are said to have a pure white colour, haze-free gloss, high hiding power and very good weather resistance; very clear colour shades are achieved in mixtures with coloured pigments. The pigment is also said to be particularly suitable for air drying and stoving paints.

Emulsion paints pigmented with Hombitan R 522 are described as having high brightness, neutral tone, high optical efficiency and very good resistance to chalking.

*Reader Enquiry Service No. 36*

**Flame detection**

The risk of a small outbreak of fire developing into a major conflagration is a constant source of concern in areas where highly inflammable materials are stored.

A safeguard against such an occurrence is provided by an ultraviolet flame detection system just developed by General Monitors UK Ltd.

Comprising a compact controller for rack, panel or wall mounting, together with remotely-located UV flame detectors, the system gives visual warning and alarm signals of flame presence by means of flashing lights on the control unit. The controller may also be wired to give automatic activation of other emergency responses: complete system shut-down, sprinkler system, fire authority alarm, etc.

*Reader Enquiry Service No. 37*





**Mindon's new electrostatic spray gun showing double moulded barrel, delicate electrodes contained in a separate nozzle which will push into the main barrel, and liquid filled high voltage cable**

### Electrostatic spray gun with double moulded barrel

A new electrostatic spray gun has been introduced by Mindon Engineering Ltd for a variety of automatic powder paint spraying applications.

The lightweight gun features a double moulded barrel to provide additional strength against accidental damage, and delicate charging electrodes situated at the end of the gun barrel are incorporated in a separate nozzle end which pushes into the main barrel. An extension nozzle is available for coating intricately shaped parts.

Two powder deflectors of 32 mm and 20 mm diameter are supplied as standard enabling a multitude of spray patterns to be achieved. Adjustment is made from the rear of the gun by means of an insulated rod which passes through the centre of the barrel.

In addition, a lightweight liquid filled high voltage cable provides flexibility and safety in the event of the cable being severed.

*Reader Enquiry Service No. 38*

### Super Mini constant rate feeder

The new Super Mini constant rate feeder for the metering of small quantities of ingredients to a high accuracy is now available from industrial weigher manufacturer Richard Simon & Sons. The unit is suitable for both free flowing and non-free flowing materials, and meters to an accuracy of  $\pm 0.3$  per cent for most products.

The feeder is rated for throughputs of between 10 kg and 1000 kg per hour. It accurately measures the weight of material over a known length of belt and by varying the belt speed the unit compensates for material density variations to maintain a pre-set throughput.

Richard Simon & Sons has set up a special test facility at its works in Nottingham where potential customers can run a quantity of an ingredient through the unit to establish its metering performance for their particular product.

*Reader Enquiry Service No. 39*

### Portable toxic gas detectors

SKC has announced a new series of portable battery operated toxic gas detectors using the well-proven principle of colorimetric paper tape analysis. Designed as a joint venture by UK and US design teams, the instruments, known as the Autostep series, have been designed to meet UK, US and European requirements.

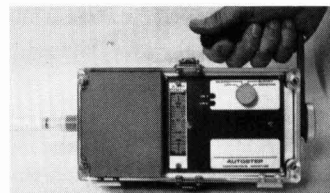
Autostep can be used in any of three different operating modes: 1. A fast response leak detector. 2. A survey instrument with direct readout in parts per million. 3. A portable area monitor for up to 36 hours continuous operation.

Fully environmentally sealed cases, rechargeable sealed lead-acid batteries and a unique dual bargraph LCD display with memory are among the many novel features of this new range.

An optional recorder module operates directly from the instrument batteries and is housed in a matching case.

Available initially as a continuous phosgene monitor, models for other toxic gases will be announced during the next six months. Examples are isocyanates, sulphur dioxide, hydrogen sulphide, hydrazine and aromatic amines. Many other gases are potentially capable of detection by the paper tape method.

*Reader Enquiry Service No. 40*

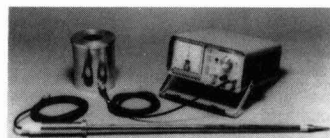


**Portable toxic gas detector, one of a new series from SKC. The instruments can be used for fast response leak detection, as survey instruments with direct readout in ppm, or as portable area monitors for up to 36 hours**

### Immersible stirrer

As a novel extension to the already established "no moving parts" Flatspin magnetic stirrer, Baird & Tatlock has developed Imspin. This is a genuine immersible unit suitable for a wide range of applications. The 12 volt fixed coil set is separate from the control unit, which is encapsulated in a resin block which is resistant to water at temperatures up to 100°C, and many corrosive materials. According to Baird & Tatlock, Imspin is ideal for stirring water baths and incubators, or for use in fume cupboards and other environments normally unsuitable for ordinary magnetic stirrers.

*Reader Enquiry Service No. 41*



**Sheen's diagnostic kit for electrostatic powder coating**

### Electrostatic powder coating diagnostic kit

Sheen Instruments is now offering a diagnostic kit for electrostatic powder coating which, it is claimed, will instantly identify many causes of poor coating performance.

The kit provides three essential measurements: the true gun voltage, the electrostatic charge on the powder and the workpiece current.

The kit consists of a portable battery operated electrometer, a high voltage probe, a Faraday cup with ion trap, interconnecting cables and an instruction guide to the interpretation of results. Two meters are available, one covering the range 0-30 kV, the other 0-100 kV.

Sheen Instruments states that the kit can control the following faults: orange peel effects, pinholes/holidays, adhesion, poor quality powder, wrong current/voltage, fused coating pull away, and back ionisation.

*Reader Enquiry Service No. 42*

### New glue gun

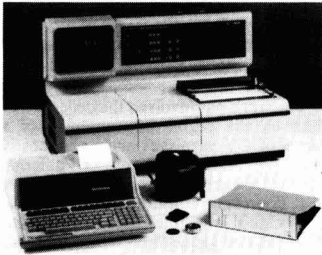
The HotFix 180 is a new competitively priced hotmelt glue gun developed by Power Adhesives Ltd.

Power Adhesives have designed the new gun around a solid state, self-regulating heater which enables it to reach operating temperature in only 3 or 4 minutes and to operate on any voltage from 100-240 volts.

*Reader Enquiry Service No. 43*



**The HotFix 180 glue gun incorporates a self-regulating heater enabling it to reach operating temperature quickly and to work on any voltage between 100-240 V**



For the laboratory involved in all aspects of colour measurement and associated UV/VIS applications, the PU 8800's large sample compartment will house a variety of accessories, for example turbid sample holders, a fluorescence unit, the integrating spheroid and a specular reflectance accessory

**New colour measurement system**

A new colour measurement system from Pye Unicam is based on what Pye claims to be the world's finest high performance UV/VIS spectrophotometer, the PU 8800. The new system, which employs an integrating spheroid and a fast, powerful software package for the HP 85 computer, is said to be the only non-dedicated system that completely conforms to the requirements of the CIE, the governing body of colour science.

With the launch of Pye Unicam's new PU 8800 Colour Measurement System, users now have the option of a system designed to meet every need, but without the expense of more inflexible, dedicated colour measurement devices.

The extensive PU 8800 range of instruments incorporates a video display, built-in recorder and printer options, and a choice of side or end-window photomultipliers. Pye claims the new system sets previously unattainable levels of user confidence and convenience, and that the PU 8800 series exploits the video concept to the full, offering new standards for speed, ease of operation and reporting of analytical results.

A unique, optional self-test routine allows the PU 8800 automatically to execute an exhaustive self-diagnosis of its operational systems.

Available on tape and disk, the software provides measurement of colour or colour difference in up to three modes: diffuse, total reflectance and transmission. Illuminants A, C, D<sub>65</sub> and D<sub>75</sub> are offered, together with an additional two illuminants of the user's own choice, all weighted at 2° and 10° observer angles.

Results are calculated in two internationally accepted forms - CIE Tristimulus values and chromaticity coordinates (X,Y,Z,x,y), and CIE LAB

76 (L,a,b,C,H.). For colour difference, all delta values are calculated and presented in addition to delta E. Reflectance data on up to 99 standards or samples can be stored on file for immediate recall and the system allows editing of stored black and white calibration values if required.

The results can be formatted in both tabular and graphical form, complete with a listing of the system and calculation conditions, operator identity and date. This allows easy storage and recall.

Perhaps the most significant feature of the equipment from the point of view of fast setting-up and data collection is its ability to name and store up to ten user programs. These programs are all complete with presentation instructions, so that by just two key strokes the user can remotely set-up and start the instrument, apply the requested colour measurement weightings to the highly accurate data, and obtain a completely formatted report from the built-in HP 85 printer.

*Reader Enquiry Service No. 44*

**Two new instruments from Byk-Mallinckrodt**

Westlairs Ltd has announced the availability of the Color and Gloss Measuring Instrument and the Blocking Tester, both from Byk-Mallinckrodt for whom Westlairs is the UK representative.

With the Color and Gloss Measuring Instrument, gloss geometries of 20°, 60° and 85° can be measured using interchangeable sensing heads or alternatively a multi-angle head covering all three.

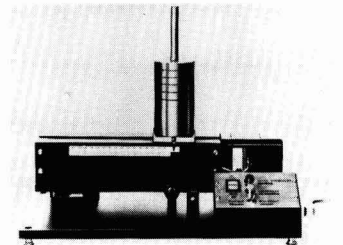
Standard colour values can be measured, and CIE LAB and Lab Hunter coordinates as well as all colour differences can be calculated. Yellowness and whiteness indices can be measured.

The instrument has a five position digital display and a built-in printer. There is a memory capacity of a maximum of 88 product standards or



**The Color and Gloss Measuring Instrument, new from Byk-Mallinckrodt. The instrument switches to colour or gloss measurement automatically according to the sensing head that is connected**

colour samples and the instrument can average up to 999 readings.



**Also new from Byk-Mallinckrodt is the Blocking Tester. This instrument will, for example, determine the force needed to free window frames which stick after being newly painted. In addition the Tester is said to be suitable for all kinds of paint film, foils and adhesives**

Based on research carried out by Rohm & Haas, the Blocking Tester will determine, for example, the force needed to free window frames which stick to their surrounds when newly painted. Laboratory procedure requires two plane test surfaces to be placed in juxtaposition and blocked under selected conditions of pressure and temperature. After this the forces necessary to unblock are measured.

The Blocking Tester is claimed to be suitable for all kinds of paint films, as well as for foils and adhesives.

*Reader Enquiry Service No. 45*

**Ultrasonic processing**

Ultrasonics Ltd has added a 900 watt ultrasonic liquid processing system to its range. This new equipment complements the well established Soniprobe and Rapidis series.

The type 7550 ultrasonic processing system is suitable for laboratory or pilot use and is capable of processing liquids at a rate of up to three gallons per minute. It is suitable for dispersion, emulsification, extraction, separation, scrubbing, leaching, mixing, disruption, disintegration, acceleration and degassing.

The system comprises a stainless steel processing cell, orifice adaptor, inlet and outlet ports, vent or pressure gauge connection and titanium horn. The cell can be incorporated in an existing processing line or system when pressure and flow rates are compatible. The ultrasonic generator used incorporates adjustable power output to control the intensity of the ultrasonic vibrations, a timer and output meter to allow exact conditions to be recorded and repeated, solid state circuitry, automatic tuning, and modular construction for ease of maintenance.

*Reader Enquiry Service No. 46*



Heraeus's instantaneous UV meter which comprises a sensor and separate indicator unit. The sensor is fitted in the accelerated weathering or light fastness testing equipment and is consequently exposed to the same radiation conditions as the specimens; the sensor is fully waterproof. The meter can also be used to measure outdoor UV levels

#### Instantaneous UV meter

Instantaneous measurement of ultraviolet radiation intensity during accelerated weathering and light fastness testing is possible using the new UV meter from Heraeus, Original Hanau division.

Measurements can be made of momentary UV radiation intensity ( $\text{mW}/\text{cm}^2$ ) as well as of cumulative radiation exposure ( $\text{Ws}/\text{cm}^2$ ) for UV wavelengths between 300 and 400 nm.

*Reader Enquiry Service No. 47*

#### New powder coating units

Three new GEMA manual powder coating units are now available from Ransburg UK Ltd. Type 701 is a single gun unit, type 702 has two guns. Each of these guns has its own control cabinet with comprehensive instrumentation and display elements for high voltage, powder throughput and the calculation of corona current. Both units are equipped with a 50 litre fluidised powder container and can be simply connected to factory electrical and compressed air supplies.

The third unit, GEMA type 705, is designed for laboratory tests and trial coatings. Its technical specification is identical to the 701, but it is intended for bench top working and has a four litre fluidised powder container.

All units are normally supplied with GEMA 100 kV manual guns. The super lightweight 70 kV mini-pistol (weighing a mere 30 ozs) can be supplied upon request.

Successful electrostatic powder coating depends, above all, on the charge applied to the particles. The higher the charge the better the results. The benefits include greater uniformity of coating thickness, reduced powder consumption and improved output. In GEMA guns the necessary high voltage is generated in the

gun itself, avoiding the voltage drop due to high voltage cables.

The control unit takes single phase AC supplies from the mains. This is converted to a 10 V 17 kHz current, which is conveyed to the gun by a 5.5 m flexible cable. The high voltage cascade in the gun delivers 100 kV at 0.07 mA (or 70 kV at 0.05 mA).

*Reader Enquiry Service No. 48*

#### IR reflecting black pigment suitable for camouflage paints

Paliogen Black L 0084 is a perylene pigment that can reflect infrared radiation and is being launched on the market by BASF. At about 650 nm the slope of the infrared reflection curve for the pigment commences to rise steeply. This property is of great significance for camouflage paints, and the pigment's green undertone in the visible range is in line with this application. Paliogen Black L 0084 is suitable for outdoor applications.

*Reader Enquiry Service No. 49*

#### Humidity controlled ovens

A new range of humidity controlled ovens has been launched by Fisons Scientific Equipment intended for use where drying to specific moisture levels is critical.

The ovens come in a wide variety of sizes. The machines have a temperature range of 20-150°C, with humidity in the 20-90°C range variable between 10-95 per cent.

*Reader Enquiry Service No. 50*

#### Refrigeration cabinets

John Godrich's range of environmental test equipment has been increased by the inclusion of the new Credit Refrigeration Cabinets. These chest type units have been designed to produce temperatures down to -40, -75 or -80°C. The standard range has 1, 4, 12, 17 and 21 cubic foot capacities. Custom sized cabinets can also be supplied.

*Reader Enquiry Service No. 51*

## literature

#### UV-cured varnishes and adhesives compatibility

The Printing and Information Technology Division of Pira has completed a study of the compatibility between adhesives and UV-cured varnishes. This is the first part of a project concerned with interactions between

adhesives and products such as ink volatiles, solvents and traces of monomer and photo-initiator which may be contained in printed paper and board.

The work has involved the collection of data on the degree of wettability of a range of UV varnishes and variations in adhesion which occur with differing degrees of cure and time intervals before test. Fourteen varnishes were used, some designated glueable and some non-glueable, and included both overprint varnishes and lacquers.

Samples were prepared with four well-cured varnishes and made into lapped joints. These in turn were subjected to stress testing to assess their tendency to fail due to creep. Adhesives which performed well in this test were used for a repeat sequence using board samples varnished in the same way but incompletely cured. The conclusions point to the wide range of surface characteristics of available UV varnishes when used under similar conditions in a project such as this.

The report "Part I: A study of compatibility between UV-cured varnishes and adhesives" is available by completing this month's reader enquiry service form.

*Reader Enquiry Service No. 52*

#### Water

The Royal Society of Chemistry recently launched the first in a new series of paperbacks aimed at students and lecturers in science. Entitled "Water", the book is written by Professor Felix Franks who has devoted much of his life to the study of water and is now regarded as one of the world's leading authorities on the subject.

An understanding of the behavioural properties of water is fundamental to gaining an appreciation of many scientific processes and principles. In the book, Professor Franks considers the present state of our knowledge of liquid water, its remarkable physical properties, its structure, and its involvement in chemical reactions. Science students at a tertiary level will find "Water" not only interesting reading but also of considerable relevance to their studies.

Future titles in the series are planned to include the topics of "Corrosion", "Catalysis" and "Food chemistry". Each book will be on a specific subject and written by an expert in the field.

At £2.50 per copy the books are exceptional value for money. They are attractive in both price and content to undergraduates and post-graduates alike and provide scientists in general with a refreshing new look at difficult subjects.

*Reader Enquiry Service No. 53*

# OCCA-35 EXHIBITION

## 1-3 May 1984

### Cunard International Hotel, London

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#### NEW CONCEPT EXHIBITION – PACKAGE DEAL FOR EXHIBITORS

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##### Lecture series

Since the Invitations to Exhibit were despatched in July a number of applications has been received from exhibitors wishing to participate in the lecture series. It is stressed that the series of lectures given by exhibitors at the OCCA Exhibition, which was introduced very successfully at OCCA-34 in 1982, is in no way intended to be a conference on a set theme but is purely an **extension of exhibition facilities**, allowing exhibitors to give talks on subjects of their own choosing. These can be of a commercial or technical nature or relate to the future development programmes of the exhibitors concerned, the object being to draw attention to particular aspects which the exhibitor wishes to promote and to allow for further discussion with interested visitors on the relevant stand. The Association will make the arrangements for the lecture series without charge to the exhibitors, but all visitors wishing to attend lectures will be asked to apply for tickets at the Information Centre – the list of those attending each lecture will be made available on request only to the relevant exhibitor. It will be appreciated that the number of lectures which can be arranged in the three day period is necessarily limited and exhibitors who have not yet sent in an application form for inclusion in the

lecture series are urged to do so without delay. It is not necessary at this stage to give the full title and summary of the proposed lecture, but an indication of the provisional title should be included on the application form in the space provided. The list of lectures will be published in the *Journal* in due course and, as in 1982, it will be possible for readers of the *Journal* to complete a form and send this in advance to ensure places at particular lectures, though tickets have to be collected from the Information Centre not less than half an hour before the stated time of the lecture.

##### Special advertising rates

A further facility which is being offered as part of the package deal to exhibitors at OCCA-35 is the opportunity to advertise at 50 per cent of the normal space booking rate in the April 1984 issue of *JOCCA* which will include the *Official Guide* to the Exhibition; no separate *Official Guide* will be issued on this occasion. All members and subscribers to the *Journal* will, therefore, receive a copy of the *Official Guide* well in advance of the Exhibition since it is scheduled to despatch the April issue before the end of March 1984. Non-members attending the Exhibition will be charged £3 admission fee which will include the cost of a copy of the April issue of the *Journal* plus

VAT. Exhibitors will understand that the advertising rate applicable will be directly dependent upon the number of advertisements which they place during the year since the Association operates concessionary rates for 3, 6 and 12 insertions.

##### Free standing space

some exhibitors have expressed a desire to have free standing space, ie space only, as distinct from either stands or complete rooms, and the Association has made arrangements on this occasion for free standing space at £50 per square metre in the Drake Suite on the mezzanine floor near the lecture hall. The free standing space is either 3 metres or 4.5 metres deep and the length of the stand would be at the choice of the exhibitor; the floor in the Drake Suite is carpeted.

Any company requiring further copies of the Invitation to Exhibit and the Question & Answer leaflet, which was circulated with the Application form in July, should apply to the Director & Secretary, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, UK, Telephone 01-908 1086, Telex 922670 (OCCA G).

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## bri news

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The standards listed below are available from: The Sales Department, British Standards Institution, Linford Wood, Milton Keynes MK14 6LE, Tel: Milton Keynes (0908) 320033, Tlx: 825777.

##### New publications

BS 1000(661):1983  
UDC 661 Chemical products  
Gr 8

BS 1000(662):1983  
UDC 662 Explosives. Fuels  
Gr 8

The above publications are now available. Copies are obtainable from the address

shown in this section's heading; the BSI should be contacted regarding price.

##### British Standards

3900:  
Methods of test for paints  
3900: Part B3: 1983 Determination of "soluble lead" in the solid matter in liquid paints: method for use in conjunction with The Control of Lead at Work Regulations, 1980 (SI 1980 No. 1248) 8 page A4 size Gr 3  
Details the procedure for determining the amount of lead soluble in hydrochloric acid of defined concentration. Method is compatible with that given in Appendix 2

of the approved code of practice "Control of Lead at Work" issued by the Health and Safety Executive in conjunction with SI 1980 No. 1248. Supersedes BS 3900: Part B3: 1965. (ISBN 0 580 11901 7)

##### Amendments

2015: 1965  
Glossary of paint terms  
Amendment No. 1 Gr 0 AMD 4332  
4289:  
Methods for the analysis of oilseeds  
4289: Part 2: 1981 Determination of impurities content  
Amendment No. 1 Gr 0 AMD 4317

**Special announcements**

BS 2782: 1970 Methods of testing plastics

The 1970 edition of BS 2782 is being revised in loose-leaf form. As various methods have been technically revised they have been circulated for public comment prior to publication in this new form. There remains a residue of methods for which no technical revision is considered necessary, but in order to complete the process it has been decided to republish these in loose-leaf form, undertaking the necessary editorial changes. The two methods given below are being treated in this way and will not be circulated for public comment.

Method 104A Cold bend temperature of flexible polyvinyl chloride extrusion compound, to be reissued as Method 151A (reference 83/53818).

Method 511A Effect of polyvinyl chloride compound on the loss tangent of polythene, to be reissued as Method 241A (reference 83/53819).

However, anyone interested in obtaining a copy of these drafts should send an A4 stamped addressed envelope to Mr R. E. Stratton at BSI Head Office quoting the reference of the document required.

**Proposed for confirmation**

5350:  
Methods of test for adhesives

5350: Part C3: 1978 Determination of bond strength in direct tension

5350: Part C7: 1976 Determination of creep and resistance to sustained application of force

5350: Part C9: 1978 Floating roller peel test

5350: Part E1: 1976 Guide to statistical analysis

**British Standards reviewed and confirmed**

3900:

Methods of test for paints

3900: Part C2: 1971 Surface drying test (Ballotini method)

3900: Part E4: 1976 Cupping test

3900: Part E10: 1979 Pull-off test for adhesion

4321: 1969

Methods of test for printing inks

**New work started**

BS 6319 Testing of resin compositions for use in construction Part 8. Method for assessment of resistance to liquids

Will describe a simple immersion method for obtaining data on the effect of chemical reagents, including water on resin compositions. CSB/20 see *Draft British Standards for public comment.*

**International new work started**

Code for designation of colours  
Will add a number code to the existing

letter code for the designation of colours in the texts of descriptions, drawings, markings etc., in the electrotechnical field. IEC/TC 16 through GEL/41

**Draft British Standards for public comment**

83/12444 DC BS 6319 Testing of resin compositions for use in construction. Part 6. Method for measurement of modulus of elasticity in compression CSB/20

83/12446 DC BS 6319 Testing of resin compositions for use in construction. Part 8. Method for assessment of resistance to liquids CSB/20

**Draft international standards available**

83/53317 ISO/DIS 862 Surface active agents - Vocabulary CIC/34

**Revised ISO Standards**

ISO 3680: 1983

Paints, varnishes, petroleum and related products - Flash/no flash test - Rapid equilibrium method 6 page D

ISO 3856:

Paints and varnishes - Determination of "soluble" metal content

ISO 3856/1: 1983 Determination of lead content - Flame atomic absorption spectroscopic method and dithizone spectrometric method 6 page D  
*No equivalent BS*

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**OCCA news**

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**Obituary****Sidney J. Reed**

For a considerable number of years, extending over the 1930s-1940s, Sid Reed was the evening class lecturer at the Hull Technical College, covering the City and Guilds courses in the chemistry and technology of paints, pigments and varnishes.

In those days there were some 30-odd paint firms of various sizes in and around the Hull area. Sid knew them all and taught the majority of their technical staff most of what they knew about paints, pigments and varnishes. He was a likeable man, very highly respected by all who knew him.

For many years he was works manager at W. R. Todd & Sons, Marfleet, and later when Todds went out of business Sid was with Blundell-Permoglaize until his retirement.

He was, of course, known much further afield through OCCA and other business connections. He was one of the founder members of the war-time Regional Group No. 21, which, in April 1943, became the Hull Section of OCCA, under the chairmanship of the late Mr G. F. Holdcroft.

From its commencement and for several subsequent years Sid was Honorary Treasurer until he became Chairman in 1949.

The 1951 OCCA Conference was held at Scarborough. It was organised and pretty well run by the Hull Section. Sid was one of those who devoted much time and effort, under considerable difficulties, in seeing this Conference successfully through.

It was a great shock to Sid when his wife, Kit, died and he was faced with the prospect of a lonely retirement. Later on, he went to one or two holiday centres and it was at one of these he met the present

Mrs Reed. They moved away from Hull, since when I lost contact with Sid.

*T. A. Fillingham*

**Newcastle Section****BTP Cup**

The 22nd Annual Tournament for the BTP Cup was played for over the Arcot Hall Golf Course, Dudley, Northumberland on Friday 3 June 1983.

Once again it was a "first time", the first time the competition had been held at this delightful course. Fourteen people competed for the trophy, which was won for the second year running by Mr J. Hall, Tioxide (UK) Ltd. The best performance by an invited guest was returned by Mr W. W. Jack, of the Scottish Section, who won a replica of the Cup.

*H. Fuller*

JOCCA



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- F45, a liquid levelling agent for powder coatings and other usual paint systems; suitable for haze-free colourless powder coatings.
- F3, a liquid levelling agent for powder coatings and other surface coatings.
- F30 P mod., a levelling agent in powder form for powder coatings.
- S4 and S6, slip and levelling agents for improved mar and scratch resistance.

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- S5, a slip and levelling agent for improved mar and scratch resistance.



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## CLASSIFIED ADVERTISEMENTS

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- ★ be between 25-30;
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- ★ be capable of negotiating – and selling – at all levels up to Managing Director;
- ★ live in or be prepared to move to the Edenbridge area;
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Salary dependent upon age and experience. A company car will be provided and there is a company pension scheme. We are prepared to help with relocation expenses, if necessary. Please write fully with CV, in strict confidence, to:

**W. B. Mayhew, Esq**  
**Sachtleben Chemie GmbH**  
**56 High Street, Edenbridge, Kent TN8 5AJ**

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## JOCCA BACK ISSUES AVAILABLE

The following back issues of *JOCCA* are available: May 1966 – December 1982 (excluding July -77 and Nov. '82, available from Sept 83 from the Association's offices). Anyone interested in obtaining these should contact Mrs K. Davidson, 31 Highburgh Drive, Burnside, Rutherglen, Glasgow G73 3RR.

**INDEX TO ADVERTISERS**

*Further information on any of the products advertised in this Journal may be obtained by completing the Reader Enquiry Service form. The Reader Enquiry Service numbers are shown in brackets below.*

<b>A</b>		
Atlas Electric Devices Co	(248)	iv
<b>B</b>		
Bentham Instruments	(267)	Cover
<b>C</b>		
Chemische Werke Hüls AG	(270)	iii
<b>D</b>		
Dynamit Nobel AG	(271)	Insert
<b>H</b>		
Henkel KGaA	(268)	v
<b>I</b>		
Introduction to Paint Technology		iv
<b>O</b>		
OCCA-35 Exhibition	(501)	ii
<b>S</b>		
Sanyo-Kokusaku Pulp Co. Ltd	(112)	iv
Silberline Ltd	(184)	Cover
Sub-Tropical Testing Service Inc	(272)	Cover

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**(OCCA G)**

*Photocopy or cut out form and send to above address.*

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General Manager,  
Sherwin-Williams Saudi Arabia Limited,  
PO Box 16665, Jeddah, Saudi Arabia*

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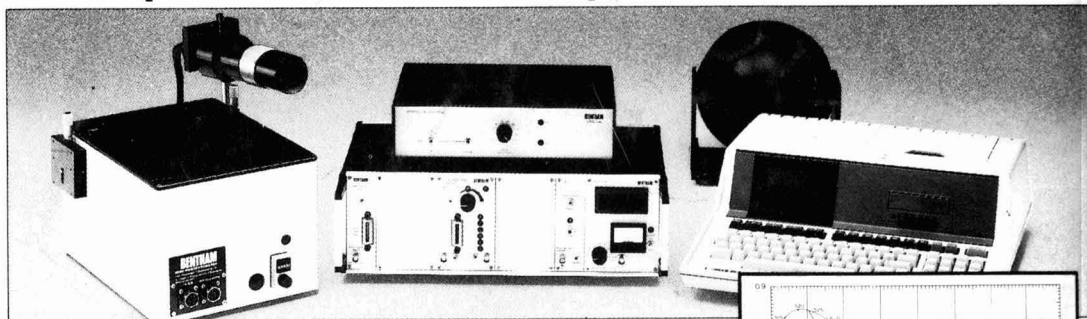
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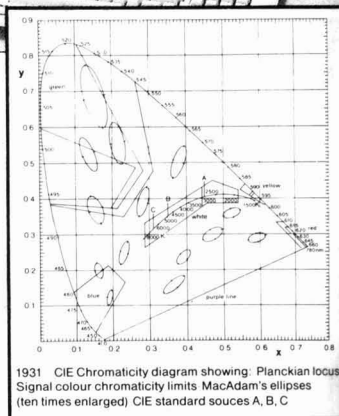
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