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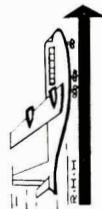
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Water-borne industrial thermosetting systems <i>H. J. Luthardt and W. Burckhardt</i>
The influence of light intensity on photoactivity in TiO <sub>2</sub> pigmented systems <i>T. A. Egerton and C. J. King</i>
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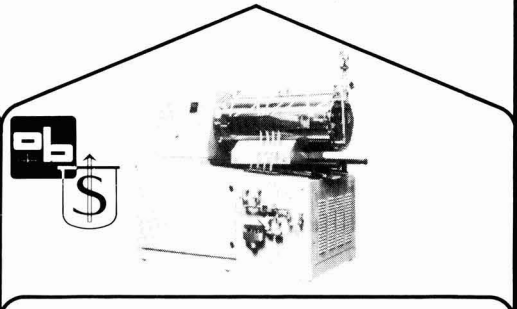
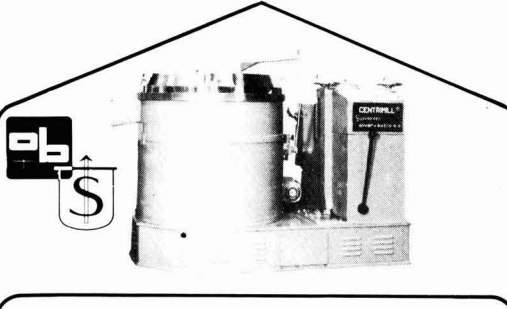
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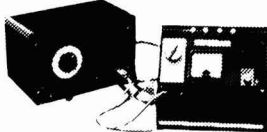
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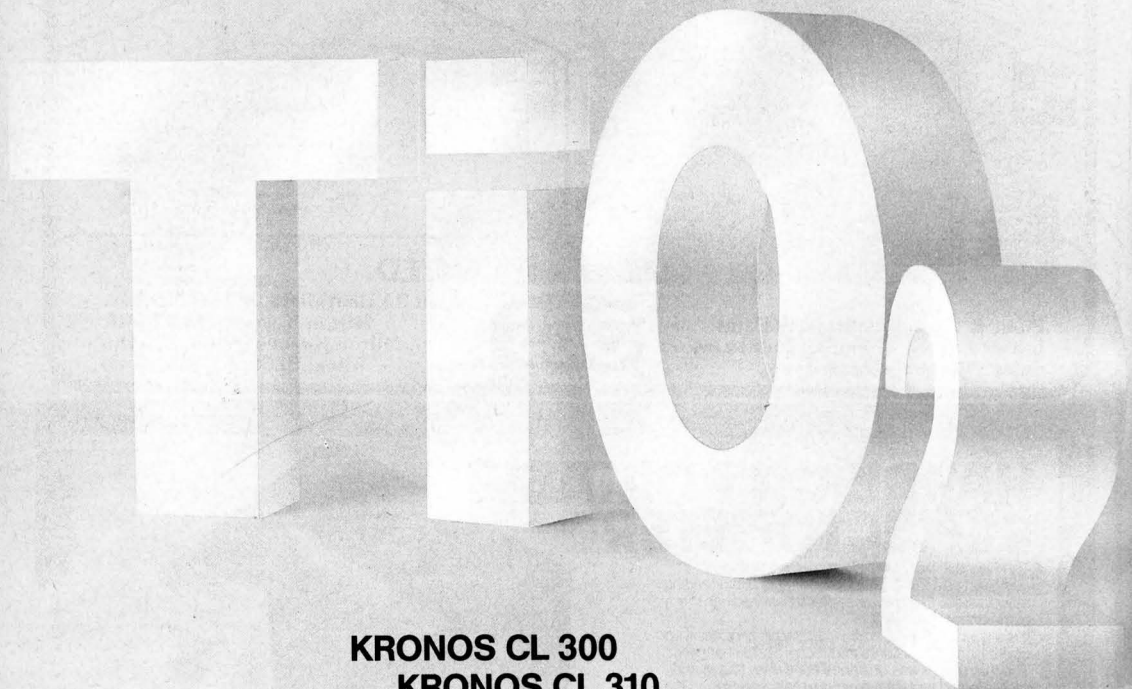
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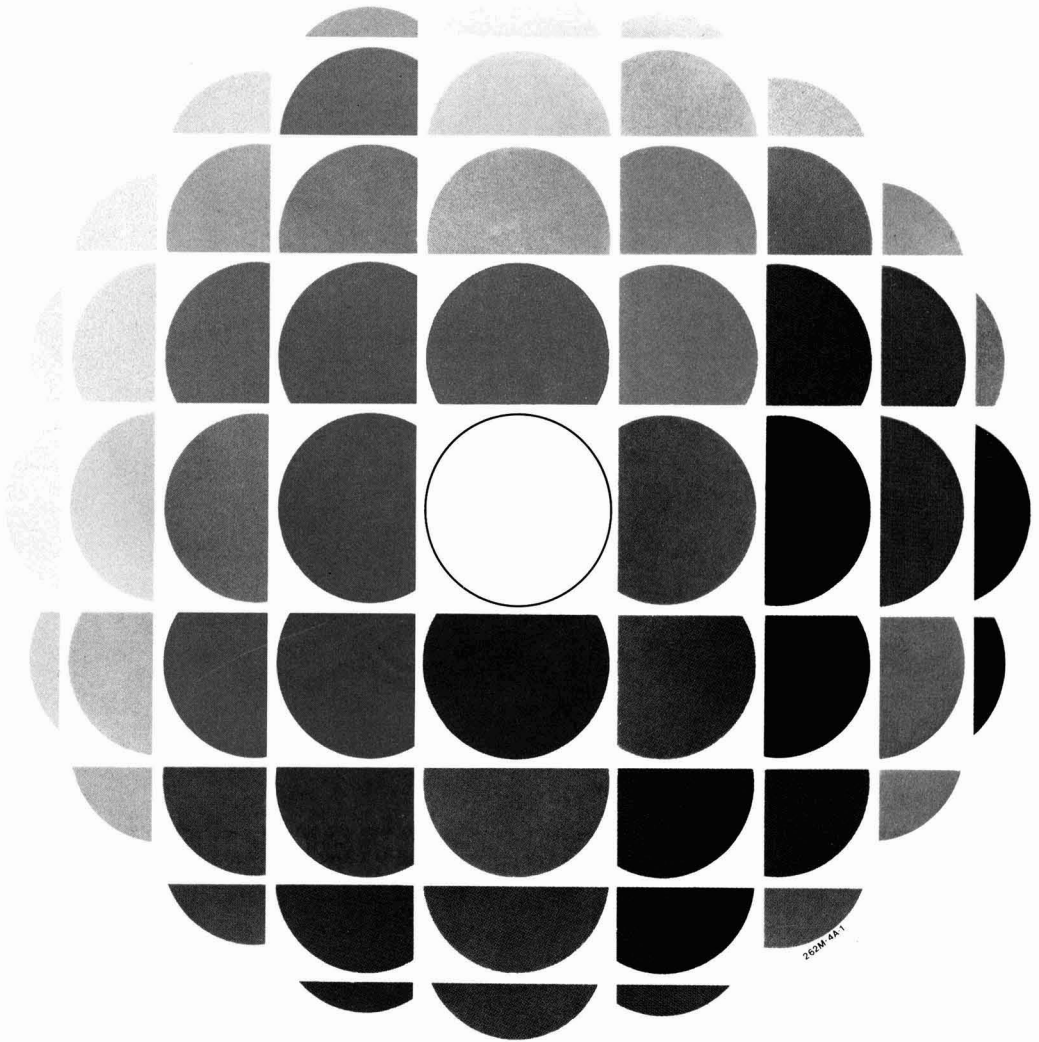
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Tel: 01-908 1086

Telex 922670 (OCCA G)

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*Transactions and Communications*

# Water-borne industrial thermosetting systems: Physical chemical behaviour of their components and aspects of application technology\*

By W. Burckhardt and H. J. Luthardt

Deutsche Akzo Coatings GmbH, Stuttgart, Germany

## Summary

Various binder types are used in water-borne thermosetting coatings systems, usually crosslinked by methoxylated melamines. In aqueous solution short-oil alkyds at a variety of concentrations under different conditions were investigated. The influence of cosolvents on their behaviour and their rheology was studied. These alkyds were also utilised as protective colloids when acrylic

monomers were copolymerised to form dispersions. The behaviour and film properties of those hybrids were studied. The melamines used showed a two fold reactivity at low and high temperature, involving solvent-cosolvent interaction.

The ease of application in hand or electrostatic spraying is demonstrated and their advantage in saving of energy is explained.

## Keywords

### *Types and classes of coatings and allied products*

water base paint  
primer  
top coat

### *Miscellaneous terms*

pollution  
cost  
energy requirement

### *Raw materials for coatings binders (resins, etc.)*

alkyd resin  
melamine resin  
melamine alkyd resin  
acrylic resin

## Les systèmes de peintures industrielles thermodurcissables à base de l'eau: le comportement physique et chimique de leurs constituants et les aspects de la technique d'application.

### Résumé

On utilise divers types de liants qui sont reticulés en général par les mélamines méthoxylées, dans la fabrication des revêtements thermodurcissables à base de l'eau. On a étudié les alkydes courtes en huile à une gamme de concentrations en solution aqueuse et sous de différentes conditions. On a étudié l'influence qu'exercent les co-solvants sur le comportement et la rhéologie de ces résines. Elles étaient utilisées également en tant que colloïdes protecteurs où des monomères acryliques étaient copolymérisés afin de préparer

des dispersions. On a étudié le comportement de ces hybrides et les caractéristiques de leurs films. Les mélamines utilisées ont démontré une double réactivité qui dépend de la température et qui entraîne une interaction solvant-cosolvant.

On démontre la facilité d'application soit par pistoletage à main ou par électrostatique, et on explique leurs avantages au point de la conservation d'énergie.

## Wässrige, wärmehärtbare Industrielacksysteme: physikalisch-chemisches Verhalten und Gesichtspunkte der Anwendungstechnologie.

### Zusammenfassung

In wässrige wärmehärtenden Anstrichsystemen werden verschiedene Arten von Bindemitteln verwendet, die üblicherweise mit methocilierten Melaminen vernetzt werden. Kurzölige Alkyde wurden in wässriger Lösung in verschiedenen Konzentrationen und unter verschiedenen Bedingungen untersucht. Der Einfluss von cosolvens auf ihr Verhalten und Rheologie wurde geprüft. Diese Alkyde wurden auch als Schutzkolloide benutzt, wenn Akrylmonomere zwecks Bildung von

Dispersionen copolymerisiert wurden. Verhalten und Filmeigenschaften dieser Mischlungen wurden untersucht. Die benutzten Melamine zeigten bei niedriger und hoher Temperatur verschiedene Reaktivität, wobei solvens-cosolvens-wechselwirkungen mitspielen.

Die leichte Anwendbarkeit sowohl durch Hand- als auch elektrostatisches Spritzen wird gezeigt, und die Vorteile dadurch möglicher Energieersparnis erklärt.

### Introduction

Water-borne systems for application in industrial stoving paints are one of three types of classical solvent based paints currently being developed. Within the range of known water-borne coatings systems, three different types can be distinguished regarding their physical state, namely dispersions, solutions, and hybrid systems.

Dispersion types contain particles of very different sizes, for example very small as in hydrosols (0.05-0.5  $\mu\text{m}$ ) or in ordinary dispersions (0.1-1  $\mu\text{m}$ ) and they react either by self-crosslinking or by crosslinking with a hardener such as a

methoxylated melamine. The flow behaviour of dispersion types on spraying vertical surfaces was found rather unfavourable.

The rheological behaviour could not be influenced until recently by the addition of thixotropic agents to overcome these difficulties. These agents also tend to cause other disadvantages. Pure solution types such as short oil alkyds were found to behave far better, and no major application difficulties were found in various formulations and over a wide range of film thicknesses. For this reason the short oil alkyds will be considered first, followed by investigations on a hybrid system. The special role of methoxylated melamines

\*Paper presented at the Association's Conference held at Stratford upon Avon from 20-23 June 1979.

as crosslinkers will be covered later, and finally the advantages in the application technology of aqueous thermosetting systems will be briefly reviewed.

### The behaviour of short oil alkyds in solution

An alkyd resin can be considered as a blend of oligomers, resulting in a more or less broad molecular weight distribution. In aqueous solvent it contains ionisable groups, able to dissociate into polyvalent macro-ions. The source of the characteristic properties of these charge carrying chains was identified as strong electric interaction between macro-ions and their counter ions. This interaction can be influenced to a large extent by the dielectric constant of the solvents. This will be explained by some examples.

### Behaviour of short oil alkyd in highly concentrated solutions

*Ref. 1*

On thinning down a nearly 70 per cent solution of alkyd A, dissolved in organic water-miscible solvents only, 95 per cent neutralised with dimethyl ethanol amine (DMEA) (the amine is considered as a solvent and is included in the organic part), a very characteristic steep slope is seen at first, followed by a rather broad field of hardly changing viscosity. On further thinning a slight viscosity increase occurs, a phenomenon which was described some time ago in the literature<sup>1</sup>. Only at rather low solids content ( $\leq 30$  per cent solids) on further thinning with water does the viscosity of the alkyd solution drop again considerably. This is shown in Fig. 1.

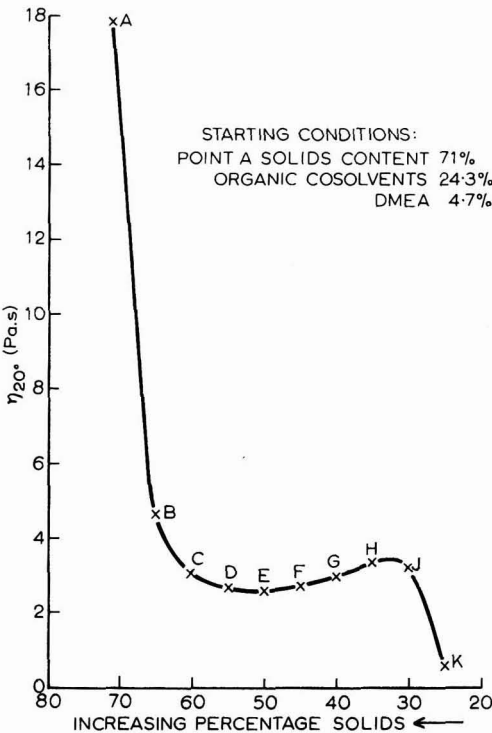


Figure 1. Thinning curve of short oil alkyd A

Table 1  
Measuring points within the thinning curve:

Points*	solids content (%)	viscosity (Pa.s)
A	71	17.85
B	65	0.466
C	60	0.305
D	55	0.269
E	50	0.259
F	45	0.271
G	40	0.295
H	35	0.333
I	30	0.319
K	25	0.055

\*See Figure 1.

This thinning behaviour of highly and medium concentrated alkyds or polyester solutions has been explained in the following way:

The increased ionic repulsion between the anions of the polymer chains leads to increased molecular dimensions and micelle formation due to further interaction of hydrophobic segments with increasing water content.

Similarly, the increase is shown when the viscosity of alkyd A at 20°C is plotted against various ratios of butylglycol/water, in Figure 2.

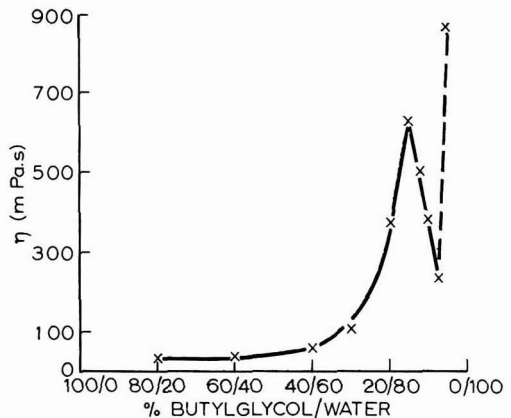


Figure 2. Viscosity of alkyd A at 20°C ( $\alpha = 0.95$ ) as a function of the ratio ethyleneglycolmonobutylether to water

Experimental points	Viscosity (m Pa.s)	Experimental points	Viscosity (m Pa.s)
1	26	7	629
2	33	8	501
3	38	9	380
4	60	10	234
5	104	11	865
6	374		

### Behaviour of short oil alkyds at very low solids content

*Refs. 2-5*

In order to obtain full confirmation of the theory that short oil alkyds in water behave like polyelectrolytes<sup>2</sup>, viscosity measurements have been carried out at very low concentrations e.g. between 6 and 0.25g per 100cm<sup>3</sup>. Very few references to this can be found in the literature.

In organic solvents, Batzer<sup>3</sup> investigated the dependence of the reduced viscosity on the concentration of linear and branched polyesters.

In various organic solvents and cosolvent-water mixture Karyakina *et al*<sup>4</sup> reported on the dependence of the reduced viscosity as a function of concentration for alkyd resin solutions.

The authors' investigations were carried out with alkyd B, neutralised to 95 per cent with N, N-dimethylethanolamine. Figures 2 and 3 show the dependence of the reduced viscosity as a function of  $c$  for alkyd B in aqueous solution or *n*-butanol respectively.

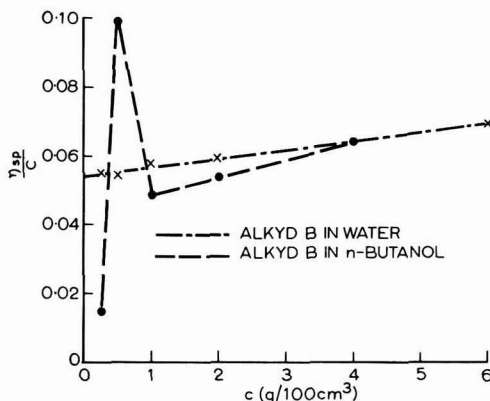


Figure 3. Dependence of reduced viscosity as function of concentration of alkyd B in water and *n*-butanol

This confirms the findings in reference 4, that the nature of the solvent has a considerable effect on  $[\eta]$ . The highest intrinsic viscosity was found in ethyleneglycol monobutylether, whereas the lowest was found in *n*-butanol.

The addition of a neutral salt is known to influence, from the behaviour of polyelectrolytes, the viscosity in a characteristic way. Recently Lehtinen<sup>5</sup> has used this approach to support the view that poly (hydrazoisophthaloyl) in the enolized form with  $\text{Na}^+$  or  $\text{NH}_4^+$  as counter ions behaves as a polyelectrolyte:

In the presence of 3 per cent LiCl/100ml polar solvent, the inherent viscosity  $\eta_i$  slightly increased with decreasing polymer concentration.

The experiment was repeated using the alkyd solution in *n*-butanol, and the same amount of LiCl, but this viscosity effect could not be found. It is concluded that a typical polyelectrolyte behaviour for this type of alkyd in this particular solvent could not be proved.

#### Viscosity behaviour on storage at moderate temperatures as a function of time

Refs. 6, 7

The viscosity behaviour over a long period of time of dissolved alkyds after neutralisation in water was followed at temperatures between 20° and 95°C. The reason was to exclude those types which are insufficiently stable in a pH-range between 7.5 and 8.5. A quick test giving a characteristic

value of hydrolytic stability of a 10 per cent resin solution kept at 95°C in a closed system was developed. By this approach hydrolytically stable alkyds for the specific purpose were sorted out. Their change of pH within a fortnight at 50°C averaged 0.8-1 pH units.

Although according to these experiments the alkyd types selected for viscosity behaviour studies were hydrolytically stable, a number of strange observations were made<sup>6</sup>. Unexpectedly and at first inexplicably sometimes strong viscosity increases up to formation of a gel and sometimes only a minimal viscosity increase occurred. Fig. 4 gives a general view of the area of viscosity changes, which could repeatedly be obtained.

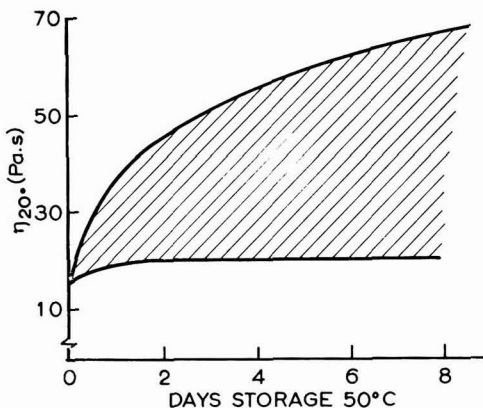


Figure 4. General area of viscosity changes of alkyd resins in aqueous solution ( $\alpha = 0.95$ )

The key for the practical solution of this viscosity instability was obtained from the observation that a test series containing one particular alkyd resin at a constant solids content and degree of neutralisation depended in its viscosity increase only on the ratio water/cosolvent; the more cosolvent used, the less increase was observed. Fig. 5 represents the results.

On the other hand, the type of cosolvent at constant solids content and constant water/cosolvent ratio also had a strong influence on the viscosity increase. This is shown in Fig. 6.

On searching for an explanation for these phenomena consideration must be given to the effect of interactions among ionised groups, counter ions, solvent and cosolvent molecules of polyelectrolytes.

Although in the case of the alkyds no really high charge density of the macro-ions exists as in, for example, poly (acrylic acid), and no salt-effect could be found, a small difference in the interactions caused by a small change of the dielectric constant,  $\epsilon$ , obviously affects the behaviour of flexible chains. Size and shape depend on charge and interaction with the counter ion, resulting in viscosity changes.

The alkaline solution of stable alkyds in an aqueous medium could have the character of a "polysoap", being able to emulsify other polymer particles in dispersion form<sup>7</sup>. As a thermosetting polymer, it could be built in by crosslinking, together with an emulsified thermosetting copolymer. So on spraying it might be possible to have the advantage of

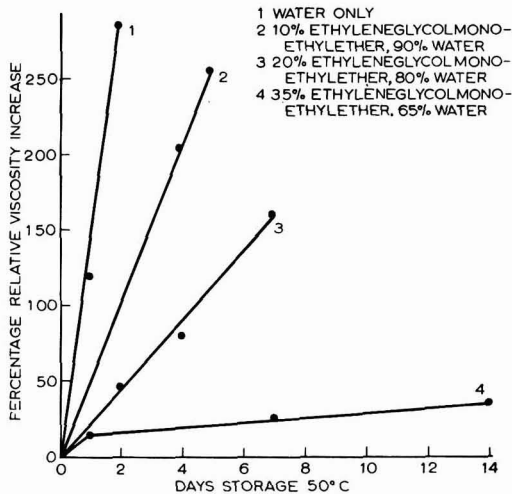


Figure 5. Viscosity changes as a function of cosolvent-water ratio (50° storage)

rheological properties of a solution together with an increased solids content because of the dispersed thermosetting component.

These considerations led to experiments, whereby a system consisting of dissolved alkyd resin, stabilising an acrylic copolymer dispersion, and being crosslinked by a methoxylated melamine was developed.

### Preparation and use of hybrid systems

#### Water soluble alkyd resin as a protective colloid for acrylic copolymer dispersions

Refs. 8, 9

The preparation of polymer dispersions in an aqueous system in the presence of a polymeric water soluble stabiliser has been described several times<sup>8</sup>. Very little literature exists which describes thermosetting hybrid systems using a water-thinnable amino resin as crosslinker<sup>9</sup>. The difficulty of making a completely compatible three component system is obvious. However, the use of hydrolytically stable resins in solution as a protective colloid seemed to be attractive enough to warrant some experiments.

#### Preparation and characterisation of the hybrid

Using a number of alkyd resins which are stable in aqueous solution, a standard mixture of acrylic monomers was polymerised in the usual way. The methods of preparation are given in Appendix 1. Bis (azoisobutyronitrile) was used in standard amounts as the radical initiator. The conditions are summarised in Table 2 and, in most cases, were kept constant in order to minimise the number of variables.

The major characteristics of the hybrids obtained were recorded in Table 3.

Analytically, the hybrids were characterised by determining  $M_n$  and  $M_w$  and the polydispersibility ratio. The results are summed up in Table 4.

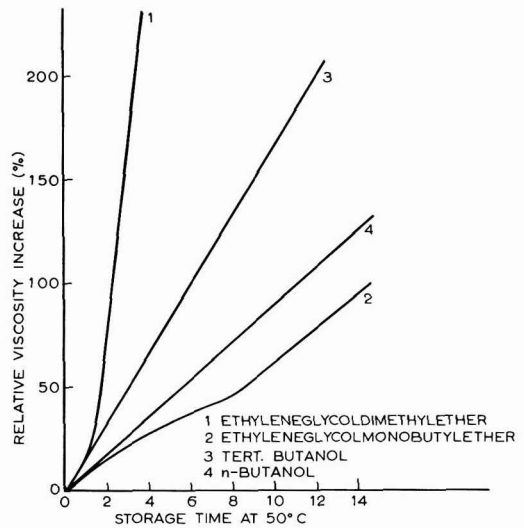


Figure 6. Viscosity increase as a function of cosolvent type

Table 2  
Conditions of a typical experiment

Solids ratio alkyd-acrylic monomers:	1:1	
Percentage cosolvent calc. on alkyd	: 25%	butylglycol
Percentage initiator calc. on monomers	: 0.63%	Bis (azoisobutyronitrile)
Dosage time monomers and initiator	: 90 min.	
Degree of neutralisation calc. on sum of acid numbers alkyd + acrylate	: $\alpha = 1.25$ (DMEA)	

Table 3  
Major characteristics of a hybrid system investigated

<i>Alkyd part</i>	Characteristics of alkyd used for preparation of a hybrid system:				
	acid number	:	45.0		
	OH-number	:	100		
	solubility parameter	=	10.65		
	$M_n$	=	2000		
<i>Hybrid</i>	Characteristics of four typical systems, using the mentioned alkyd as protective colloid:				
Batch no	External emulsifier*	Viscosity † 20°C (Pa s)	pH (final)	Solids content	
53	--	not determ.	8.03	39.2	
58	3%	0.696	7.69	39.8	
59	3%	0.906	7.58	39.6	
67	3%	6.90	8.10	38.6	

\*Trade mark "Serdex NNP 13" by Servo B. V. Delden, Netherlands.  
†Viscosity measurements with an "Epprecht" Rheomat 15.

#### Investigations of the influence of other parameters on properties of the hybrids

A large number of variables have an influence on the final properties of the product. A few characteristic ones which



were investigated are summarised below:

1. The solids ratio alkyd/acrylic monomers especially with regard to optimisation of the stabilisation effect.
2. The necessity of using an external non-ionic emulsifier. This helped to decrease the viscosity of the final product.
3. The composition of the alkyd resin and variations in  $M_n$ .
4. The type and quantity of initiator to influence  $M_w$  of dispersion.
5. The degree of neutralisation and its influence on the stability of the dispersion.
6. The type of water miscible cosolvent.
7. The chain transfer agents and their effect on  $M_w$ .

Table 4  
Analytical characteristics of the four types of hybrids

Batch no	$M_n$ disp. matter	$M_n$ alkyd	$M_w$ disp. matter	Polydisp. ratio
53	32 900	2000	220 000	6.7
58	35 200	2000	237 000	6.7
59	36 900	2000	238 000	6.4
67	18 900	2000	167 300	8.9*

\*In this case 1% of laurylmercaptane was used calc. on acrylic monomers.

Analytical determinations by GPC using Styragelcolumns ( $3 \times 10^4$ ,  $10^4$ ,  $10^3$ ,  $10^2$  Å) and methyl ethyl ketone as elution solvent.

#### Paint technological investigations

White paints to a standard formulation were prepared (Red Devil) and applied by spraying horizontally and vertically on bonderised steel plates (Bonder 130). The standard formula is given in Appendix 3. The spray viscosity varied between 20 and 35 sec.; the solids content between 40 and 50 per cent, but, generally, a viscosity of 30 sec. is desirable.

The detailed results of evaluation can be found in the Appendices 4 and 5.

#### Elasticity-hardness balance

In the first samples, elasticity (according to Erichsen) normally remains at a very low level ( $< 1.0$ mm) and the König hardness remains around 133–138 sec. The last samples indicate an improvement of elasticity (average  $> 7$ ) at the expense of hardness (100–130).

#### Viscosity stability tests

Only a few stability tests at 50 have, as yet, been investigated. With the white standard formulation only a slight increase was found during the first four days. After one week, however, viscosity had increased by 160 and 330 per cent respectively and after two weeks the samples had gelled.

As these test results indicate, it has been shown that hydrolytically resistant short oil alkyds can be used as protective colloids to stabilise a thermosetting acrylate-styrene copolymer dispersion, and to crosslink it by using methoxylated melamines. Glossy films with good average properties can be obtained. Aspects of application technology of this type are mentioned later in this paper.

For the short oil alkyds in solution, as well as in the hybrid systems mentioned, various methoxylated melamines have been used for crosslinking. These types of melamine resins dissolve completely in water and contribute in their own way

to the overall behaviour, especially on storage at room and elevated temperatures. It might be worthwhile considering this special contribution in order to complete the understanding of the aqueous systems.

#### The role of methoxylated melamines in aqueous systems

Refs. 10, 11, 13, 14

On diluting a commercial hexa methoxy methyl melamine (HMMM) with water (assumed solids content 100 per cent) a viscosity plot considerably different from those of the alkyds or other water-thinnable polyesters or acrylics is obtained. This indicates a more linear relationship between viscosity and solids content (see Fig. 7).

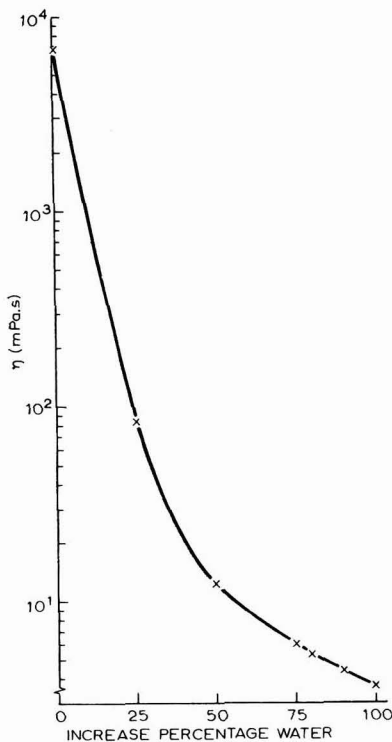


Figure 7. Thinning curve of a commercial HMMM with water (20 C)

The most probable reason for this is that HMMM as a non-ionic low molecular weight substance is capable of forming hydrogen- and dipole-dipole bonds with water. An increase of molecular dimensions due to ionic repulsion or micelle formation is not possible. With the alkyd resin, water plays the role of a "semi-solvent", i.e. a real solvent only for the hydrophilic parts. The hydrophobic parts (e.g. hydrocarbon chains from fatty acids) are solubilised by the water miscible cosolvents (e.g. n-butanol).

It can be seen that HMMM acts in the same way as n-butanol as regards its influence on the viscosity of different

blends with increasing HMMM content, as indicated in Fig. 8.

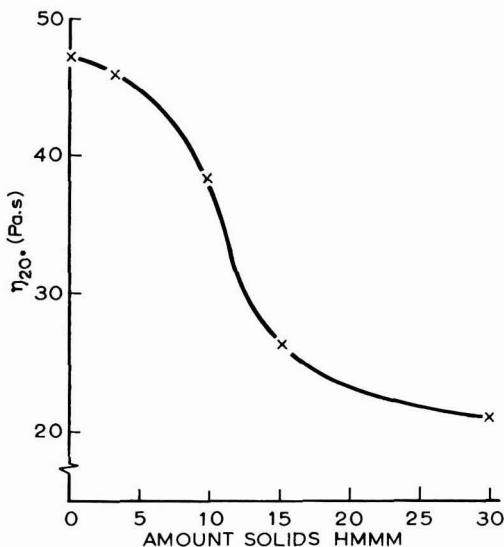


Figure 8. Viscosity of different blends of alkyd C ( $\alpha = 0.95$ ) with a commercial HMMM

At first sight, the solution of HMMM in an alcohol used as cosolvent seems to be relatively stable. For example, the viscosity and pH-changes of a commercial HMMM dissolved at 65 per cent in n-butanol and stored at 50°C for a fortnight has been followed. The changes are shown in Fig. 9.

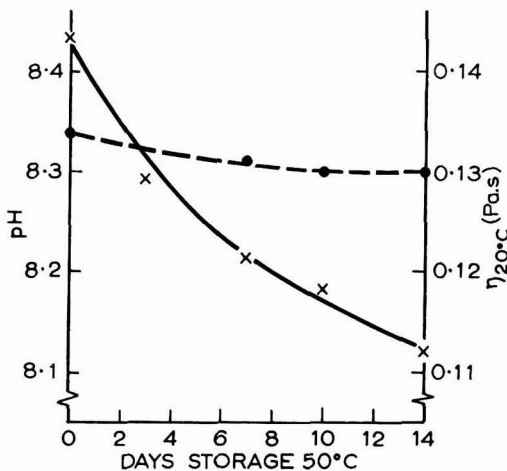


Figure 9. Changes in viscosity and pH of a sample of commercial HMMM 65 per cent in n-butanol

However, the same resin dissolved in water and stored under identical conditions shows far more dramatic changes, as can be seen in Fig. 10.

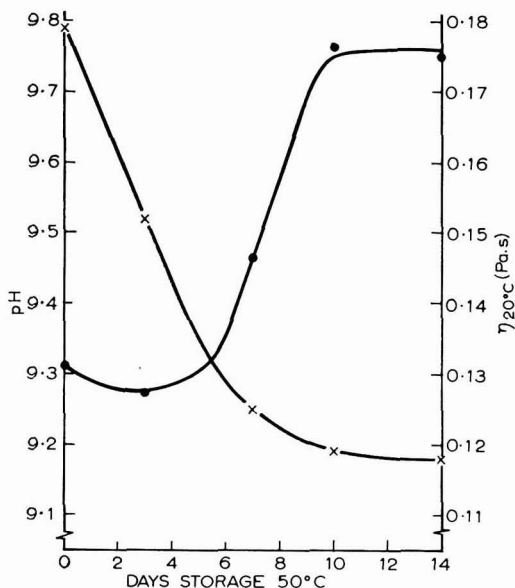


Figure 10. Changes in viscosity and pH of a sample of commercial HMMM 65 per cent in water

This could indicate that fundamental changes on molecular scale could occur during that period under the test conditions, which are derived from "paint conditions": The paint would have the same pH conditions and would be stored at the same temperature for the same period.

The examples above contained the HMMM alone, either in pure cosolvent or pure water. Under real conditions, a blend would be present, and a large number of competitive reactions could take place.

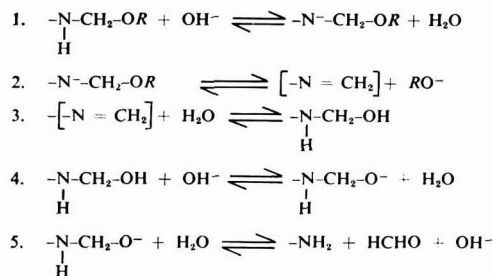


Figure 11. Decomposition of HMMM in aqueous alkaline solution<sup>10</sup>

The various reaction steps are formulated for incompletely methylolated melamines. Analytical investigations<sup>11</sup> have clearly indicated that many commercial HMMM's usually contain some -NH or N-CH<sub>2</sub>OH groups, indicating deviations from ideality. Thus, these reaction steps in alkaline aqueous media are very probable. By means of <sup>1</sup>H-NMR, a model system alkydformaldehyde could be clearly demonstrated in n-butanol/D<sub>2</sub>O solution. The signals at 4.8 ppm were absent at the start. They appeared, however, after 4 days storage of the sample at 50°C.

Partial decomposition of HMMM in aqueous solution at the pH ratio investigated is not the only reaction path. Investigations using GPC of methylolated melamines in water at pH 7.5–8.5 with a high content of butyl glycol showed that even at room temperature after standing for a few hours, the molecular weight distribution had changed in favour of products of somewhat higher molecular weight. Their formation could be explained by nucleophile substitution by the alkoxylate ion of the cosolvent<sup>13</sup>.

Summarising, it can be seen that there is a complicated behaviour of methoxylated melamines in a complex system, consisting of a neutralised alkyd, cosolvent, and water. Rheologically HMMM, on dilution with water, behaves as would be expected for hydrophilic neutral small molecules. Thus, it is able to act itself as a cosolvent and give a considerable dilution effect on blending. When water is excluded and an alcohol used as solvent, no dramatic change in pH and viscosity could be detected. However, severe changes occur when water is used as the sole solvent. In the paint, blends of water and cosolvent will be present. Reaction of HMMM with nucleophiles such as OH<sup>-</sup> or the alkoxylate-ion become probable.

These complex reactions can occur at low temperatures before any crosslinking occurs. The mechanism of crosslinking has been very well investigated<sup>14</sup>, however, and thus needs no discussion here.

### Application technology of aqueous thermosetting systems

*Refs. 15-19*

It is evident that the present conventional handspraying and electrostatic spraying methods can be used within certain limits<sup>15</sup>. Three essential questions arise with regard to the technological problems:

1. Is a spraybooth with a controlled atmosphere necessary in order to apply this material with good results?
2. Is it possible to save energy by applying aqueous thermosetting systems?
3. What effect do these systems have on air pollution?

With respect to (1) above, the investigations by Quenzel and Mode<sup>16</sup> show that the most acceptable climatic conditions for workers in spray booths are as shown in Figures 12 and 13.

The first shows the comfort limits (temperature as a function of humidity) and the second the same limits indicating the temperature as a function of air speed.

The authors have independently investigated the application of a waterborne filler, using handspraying and electrostatic handspraying under different climatic conditions. The temperature was varied between 20 and 35°C, the relative humidity between 20 and 90 per cent. Material of identical viscosity was always applied in the same way, but special attention was paid to the tendency to sagging and pinholing as a function of layer thickness. Fig. 14 shows the overall findings.

These products can be applied within a very broad temperature/humidity range without difficulties. If the "synthetic" climate is compared with real climatic conditions over a long span of time, a statistical evaluation of data from the weather station at Hohenheim University the following picture is obtained (Fig. 15).

The number of hours over a four year period<sup>17</sup> within the

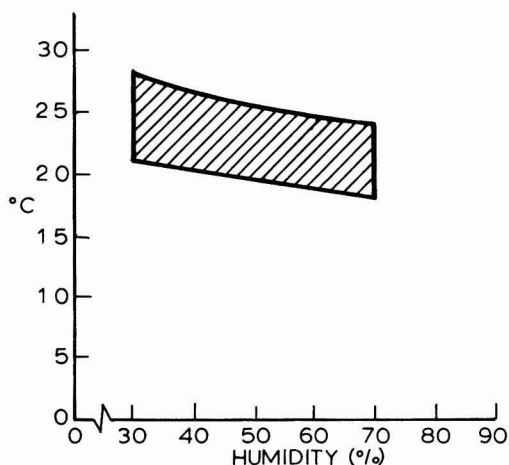


Figure 12. Area of comfort for workers. Temperature as a function of humidity

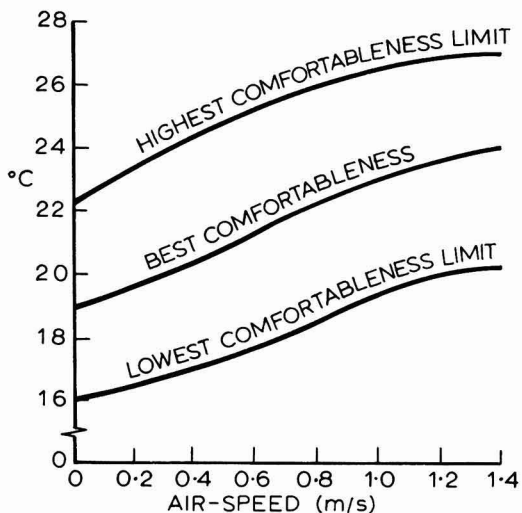


Figure 13. Area of comfort for workers. Temperature as a function of air-speed

comfort limits and the application area for the product can be seen and there is a broad area of conditions which can be brought into this field by variation of the spraybooth temperature. There remains about 22 hours in which the application of the filler mentioned could be critical. Considering the whole span of time involved, these periods are insignificant in statistical terms and can be neglected.

Although these figures are restricted to a local site (Stuttgart-Hohenheim) it is thought they represent the general central European conditions.

As a result of these investigations the authors are inclined to suggest that atmospheric control of spraybooths is not necessary when waterborne primers and primer-surfacers are

being applied. At present it is not yet possible to state whether this is also valid for water-borne topcoats (solid colours and metallics). The investigation is being continued.

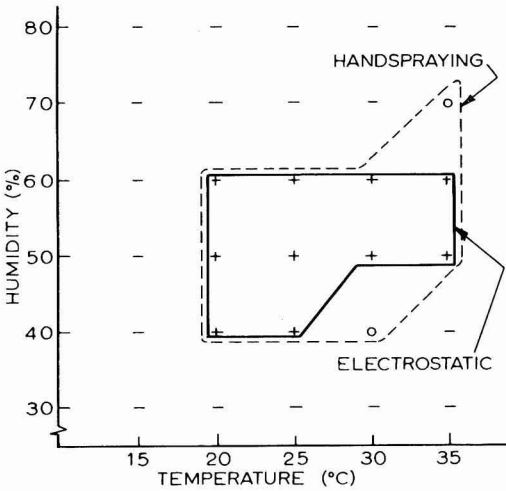


Figure 14. Application area of water thinnable filler 02-31001 using electrostatic and handspraying techniques

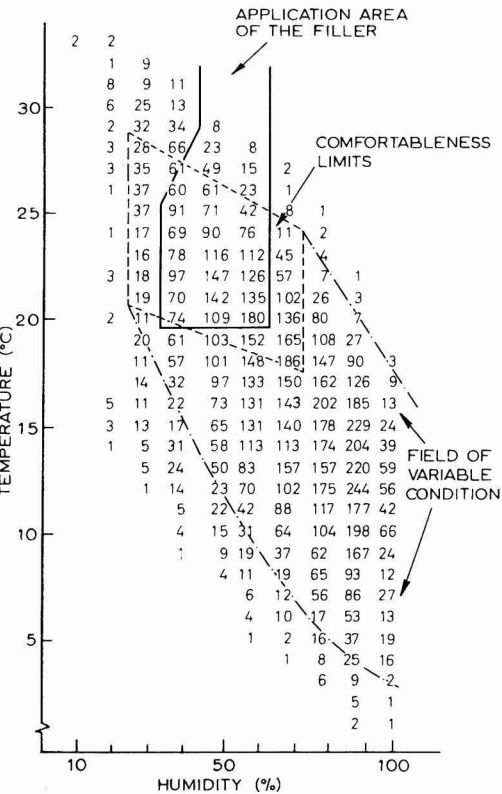


Figure 15. Statistical evaluation of climatic conditions

Another question of primary importance is whether energy is saved by applying water-borne thermosetting systems?

The automotive industry, as one of the possible major users in the future of these systems may be considered from the point of view of energy consumption.

Figure 16 shows the relative amount of energy used at various stages.

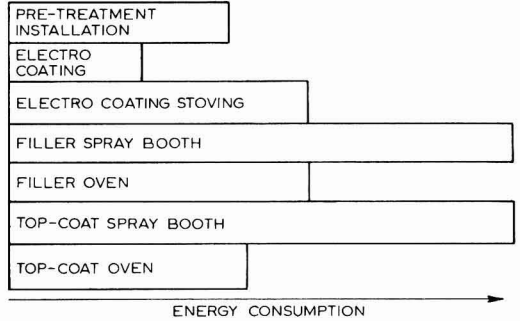


Figure 16. Comparison of energy consumption in an automotive paint shop

It can be seen that the topcoat and filler *spraybooth* need most energy followed by EC-stoving and *filler oven*. Less energy is consumed by the pretreatment installation and the topcoat oven and the least by the EC application. Some calculations which compare the energy consumption of water-based and conventional paints are shown in Tables 5 and 6.

The conclusion is that water-borne paints can be applied for about the same energy costs as for solvent based paints.

An answer now has to be found to the last question, regarding air pollution.

Novel aqueous systems in many cases contain a very low content of organic solvent e.g. 6 per cent at spraying viscosity. Here and in similar cases no afterburning should be necessary. This would affect the calculation of the overall operating expenses. However, not only solvents are liberated during stoving, but also breakdown products from the curing reaction e.g. alkyd-melamine. These products, chemically identified in a recent separate study<sup>18</sup> can cause objectionable odours.

To remove these decomposition products, simple washing techniques were used on a laboratory scale, whereby the vapours were estimated for their C-content by flame ionisation techniques<sup>19</sup>. These washings, without any addition of chemicals to the washing fluid, resulted in a complete removal of decomposition products, which means that such methods would give environmentally clean vapours.

It is hoped that the investigation described in this paper shows that waterbased paint systems can have remarkable advantages in comparison with classical solvent-based products.

Primers and primer-surfacers do not need a controlled atmosphere chamber to obtain good results. The investigations into topcoats are still proceeding.

Table 5  
Comparison of solvent based with water based systems

	A Conventional paint*	B Water-borne paint 5% org. solvent 95% H <sub>2</sub> O	C Water-borne paint 20% org. solvent 80% H <sub>2</sub> O	D Water-borne paint as C acc. to TA-Luft solv. class III
fresh air flash-off zone	8125 kg	400 kg	1625 kg	54600 kg
fresh air oven	8125 kg	400 kg	1625 kg	54600 kg
heat of evaporation flash-off zone	20930.0 kJ	134856.2 kJ	117208.0 kJ	117208.0 kJ
heating-up of the steel	552552.0 kJ	552552.0 kJ	552552.0 kJ	552552.0 kJ
heating-up of paint + solvents	42383.3 kJ	58691.9 kJ	56197.1 kJ	56197.1 kJ
heat of evaporation oven	20930.0 kJ	134856.2 kJ	117208.0 kJ	117208.0 kJ
heating up of the air	979524.0 kJ	48586.9 kJ	195904.8 kJ	6572020.0 kJ
total:	1616319.3 kJ * = 100%	929543.2 kJ = 57%	1039069.9 kJ = 64%	7415185.1 kJ = 460%

\*Energy consumption of A = 100%. The other percentages are related to A, the energy consumption of the conventional paint system.

Table 6  
Comparison of energy consumption

	Conventional paint 6 kg solvent/hr after-burning 6 kg solvent/hr	Water-borne paint 95% H <sub>2</sub> O 5% solvent No after-burning	Water-borne paint 80% H <sub>2</sub> O 20% solvent After-burning	Water-borne paint 80% H <sub>2</sub> O 20% solvent Fresh air
heating of the air				
distance of				
flash off	5.65 x 10 <sup>6</sup> kJ		1.13 x 10 <sup>6</sup> kJ	
over	4.73 x 10 <sup>6</sup> kJ		0.96 x 10 <sup>6</sup> kJ	
	10.38 x 10 <sup>6</sup> kJ		2.09 x 10 <sup>6</sup> kJ	
+ normal amount of energy	+ 1.62 x 10 <sup>6</sup> kJ		+ 1.05 x 10 <sup>6</sup> kJ	
	12.00 x 10 <sup>6</sup> kJ		3.14 x 10 <sup>6</sup> kJ	
- amount of energy for burning of solvent	- 4.35 x 10 <sup>6</sup> kJ		- 0.84 x 10 <sup>6</sup> kJ	
	7.65 x 10 <sup>6</sup> kJ 475%	0.92 x 10 <sup>6</sup> kJ 57%	2.30 x 10 <sup>6</sup> kJ 140%	7.41 x 10 <sup>6</sup> kJ 460%

Water-borne paints can be applied with about the same energy costs as solvent-based paints.

The new systems do not pollute the air because of the minor amount of organic solvents present and the decomposition products from the curing reaction can be washed out without chemical aids.

## Conclusions

The behaviour of short oil alkyds in solution at high concentrations down to very low concentrations is determined by the functional groups causing the solubility and many phenomena are due to the polar solvent water. These alkyds can be sole binder or protective colloid for a hybrid system showing some advantages compared to the pure solution.

Methoxylated melamines used to cure both types show characteristic properties of a hydrophilic, non-ionic cosolvent and crosslinker. They are liable to undergo chemical reactions while still in the pre-cure state.

Favourable aspects of the application technology are that basically no new spraying apparatus is necessary, a minimal amount of organic cosolvent is used, and freedom from air pollution if not a saving of energy is achieved.

It is considered that water-borne thermosetting systems offer an attractive and promising new technology.

## Acknowledgement

This work could not have been done without the aid of Miss A. Broos, Messrs H. van Rooijen and D. Wareman from Akzo Coatings Resin Research c/o Synthese BV, Bergen op Zoom, Netherlands. Analytical investigations were done by Mr P. Wagenaar of Synthese BV.

Mr K. Röder from Deutsche Akzo Coatings GmbH, Resin Laboratory helped with viscosity measurements and preparation of the figures. A part of the rheological measurements was made by Mr Overdiep (Akzo Corporate Research Arnhem).

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## Appendix 1

### Experimental part: Preparation of alkyd resins

The alkyd resins were prepared by esterification at 200–225°C

## Appendix 4

Batch number	Ratio acrylate/alkyd	Cosolvent in % of alkyd	Initiator related to monomers	Dosage time (hrs.)	Degree of neutralisation with DMEA	External emulsifier	20°C (m Pas)	pH	Solids content
53	1:1	25% butylglycol	AJBN 2.17%	3	1.25	no	ntm	8.03	39.2
58	1:1	25% butylglycol	AJBN 0.63%	1.5	1.25	3% Serdox NNP 13	696	7.69	39.8
59	1:1	25% butylglycol	AJBN 0.63%	1.5	1.25	3% Serdox NNP 13	906	7.58	39.6
67	1:1	25% butylglycol	AJBN 0.63%	1.5	1.25	3% Serdox NNP 13	6900	8.10	38.6

## Appendix 5

Batch number	Solids at spray viscosity	Viscosity DC 4	Film thickness	Gloss (Lange)	Evaluation Erichsen (mm)	Conical bend	Impact resistance	Hardness (König)	Adhesion on bonder
53	39.5	30	50 μm	71	0.4	10	1	170	0
58	46.5	34	50–60 μm	60	5.0	10	1	134	0
59	45	32.5	60 μm	59	1.3	10	1	138	0
67	44.2	31	55–65 μm	52	0.6	10	1	128	0

## Discussion at Stratford Conference

PROF J. KUMANOTANI asked what was the molecular weight distribution of the alkyd resin, as this had an influence on the activity of the curing reaction.

by the fusion process in the usual manner. The polycondensation was stopped at an acid number of about 44.

### Preparation of the acrylic dispersions in aqueous alkyd resin solutions

- Purge the reaction vessel with inert gas. Heat the alkyd resin and cosolvent to 90°C.
- As soon as all solids are dissolved, DMEA is added and the vessel is kept for 15 minutes at 90°C.
- Addition of water (demineralsised); content is kept at 80°C.
- Addition of emulsifier and about 15 per cent of the total quantity of initiator.
- After 5 minutes at 80°C the mixture of monomers, initiator (about 55 per cent of the total quantity), and DMEA to neutralise the acids in the monomers plus 25 per cent are added.
- Add the remainder of about 30 per cent of total initiator.
- Keep to 80°C until a good conversion is obtained.

## Appendix 2

### Typical composition of monomers used for radical polymerisation:

15%	hydroxypropylmethacrylate
28%	methylmethacrylate
34%	styrene
22%	butylacrylate
1%	methacrylic acid

## Appendix 3

### Paint formulation used for testing the dispersions:

Resimene 2-720 (90%-solids in H <sub>2</sub> O)	22.22..gr. (80:20)
TiO <sub>2</sub> RN-59	50.0 "
2-amino-2-methyl-1-propanol	1.0 "
Dimethylethanolamine	1.0 "
H <sub>2</sub> O demineralised	20.0 "
Disperse by Red Devil (50 gr. glasspearls)	
Add resin dispersion	200.0 "
Add demin. water until spraying viscosity	
Curing temperature 30 min. 130°C.	

DR LUTHARDT stated that the distribution was completely normal for an alkyd and was in no way special. The ratio between Mw and Mn was about 4 or 5, and could be

measured easily by GPC. The only difference was the solubility of the alkyd resin.

Prof Kumantani asked if any influence of a variation in the solvent composition upon the curing behaviour of the resins had been noticed and if there were any indications of a chemical reaction during accelerated testing of the solutions.

Dr Luthardt said that several experiments had been done in this area, but no evidence had been found of any chemical reaction taking place during the testing at 40 or 50°C. The only changes noted had been in the HMMM portion, but no reaction products had been discovered, which would, for example, be the case when using butoxylated melamines. There was no crosslinking between the alkyd and the melamine.

The viscosity changes which occur upon storage at, say, 40°C depend to a large extent on the type and amount of cosolvent used; more cosolvent reducing the size of the changes. However, the aim is to incorporate the minimum amount of cosolvent for environmental reasons; it is always less than 10 per cent of the final paint formulation. Certain formulations had been made with only 6 per cent of organic cosolvent in the final paint. No variation in the reactivity had been observed due to a change in the cosolvent.

DR M. L. ELLINGER, pointed out that the paper had been primarily concerned with the rheological and application properties of these systems, and asked whether they met the durability requirements of the automotive industry.

DR LUTHARDT stated that the systems performed as well as, and in some cases better than the conventional solvent-borne systems, according to the results of exposure tests conducted in Florida and Europe.

MR S. VOUT asked if these hybrid systems had yet achieved any commercial utilisation in Europe.

DR LUTHARDT answered that as yet the products were not being used commercially in Europe or in America, but they were covered by several patents, as given in the references.

MR R. J. KING referred to Figure 16 of the paper, which gave the relative power requirements for the various stages of the process. In his experience, the item with the largest power requirements was the stoving process and not the spray booths.

DR LUTHARDT pointed out that if the energy requirements of the pretreatment, electrocoating and the EC dryer were added, the figure obtained would be larger than that for the spray booths.

Mr King suggested that the spray booth figure might include the energy requirement for pre-heating the air, which could be a very large amount.

DR W. FUNKE pointed out that no significant influence of humidity and temperature on the applicational properties had been found with these water-borne fillers. He contrasted this with results obtained with low-pigmented top-coats from various commercial binders, which showed significant differences in sagging and flow properties, especially at elevated humidity and temperature.

DR LUTHARDT stated that this was in agreement with work that had been carried out with fillers which contained an organic cosolvent. However, in this work a special filler material had been used which contained no cosolvent, but only water. They had investigated this at high humidities and temperatures, and the results were surprising because the influence which they had expected to find occurred only to a very limited extent.

MR D. A. KALWIG asked about the suitability of this system for industrial applications where small components were coated by dipping. Many of these components contained holes, and he asked if this system was suitable for this type of object.

DR LUTHARDT said that his particular investigations had been into application by spraying, as most major components were now pretreated by this method.

MR L. D. HIGNETT noted that it was suggested that no special arrangements were needed to control the atmospheric conditions in the spray booths when the water-borne primers were being applied. He asked if this claim had been tested by spraying complete motor cars in a production line under normal line conditions and with the track in motion at the normal speed.

DR LUTHARDT agreed that there was a large difference between spraying a test panel and a complete motor car, and confirmed that several motor cars which had been sprayed under normal conditions in various factories were at the moment under test.

MR A. G. NORTH asked Dr Luthardt to compare water-borne and solvent-borne systems, because with a water-borne system, the dilution curve shows that to achieve a high enough viscosity for spray application, it is necessary to incorporate a fairly high proportion of cosolvent, and even with a 6 per cent content of cosolvent, as quoted, in the final coating formulation, when the solids content is around 30 per cent there is still a solvent content of around 18 per cent; this compares with a conventional system having 80 per cent resin, 20 per cent solvent and no water.

DR LUTHARDT said that with the water-borne system, one of the major advantages was that there was no energy requirement for after-burning and that the release of organic solvents was reduced. These types of coatings were favoured by the new legislation being introduced.

MR E. L. FARROW referred to the experimental experience in the automotive industry, where the water based thermosetting paint had been applied over an electrocoat primer. He asked if the top coat could be applied using a wet-on-wet system, and if the system could be used to apply metallic finishes, either as a single system or as a clear over base system.

DR LUTHARDT stated that a large amount of work was currently being undertaken in this area to develop a system for a metallic base coat and a water-borne clear top coat, but as yet there were still a number of problems to be solved and results were not yet available. Dr Luthardt said that several Divisions of his company were involved in developing the system for application by the wet-on-wet method.

# The influence of light intensity on photoactivity in TiO<sub>2</sub> pigmented systems\*

By T. A. Egerton and C. J. King

Toxide International Ltd, Central Laboratories, Portrack Lane, Stockton-on-Tees, Cleveland TS18 2NQ

## Summary

The correlation between natural weathering and different accelerated test methods has been discussed for many years, and it is usually assumed that the rate of paint degradation is proportional to the intensity of the incident ultraviolet radiation.

Results from studies of the photo-oxidation of isopropanol by TiO<sub>2</sub>, a reaction known to correlate well with the weathering of

paints, indicate that under the light intensities normally encountered, the oxidation rate is proportional to the square root of the light intensity. This conclusion is shown to be a consequence of the processes occurring in the TiO<sub>2</sub> crystal when illuminated by UV light.

The implications for the weathering testing of paints are discussed.

## Keywords

*Raw materials for coatings  
prime pigments and dyes  
anatase titanium dioxide  
rutile titanium dioxide*

*Processes and methods primarily associated with  
analysis, measurement or testing  
accelerated weathering  
accelerated testing*

*service or utility  
photo-oxidation  
photoactivation*

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

*Miscellaneous terms  
UV light*

## L'influence de l'intensité de lumière sur la photo-activité en systèmes pigmentés au dioxyde de titane

### Résumé

Pendant plusieurs années on a discuté la corrélation entre les résultats de l'exposition aux intempéries et ceux de diverses méthodes d'essais accélérés et on suppose en général que le taux de dégradation des peintures est proportionnel à l'intensité de la radiation ultra violette incidente.

Les résultats obtenus par les études sur la photo-oxidation d'isopropanol par TiO<sub>2</sub>, une réaction, qui on le sait, donne de bonne corrélation avec le vieillissement de peintures exposées aux

intempéries, indiquent que pour les intensités de lumière ordinairement rencontrées, le taux d'oxydation est proportionnel à la racine carrée de l'intensité de lumière. On démontre que cette conclusion est une conséquence des processus qui se produisent au sein du cristal de dioxyde de titane lors de l'irradiation par la lumière ultra violette.

On discute l'importance de ces études à l'égard des essais de résistance des peintures aux intempéries.

## Der Einfluss von Lichtintensität auf die Photoaktivität von mit Titandioxid pigmentierten Systemen

### Zusammenfassung

Die Korrelation zwischen natürlicher Bewitterung und verschiedenen künstlich beschleunigten Prüfmethoden wurde seit vielen Jahren diskutiert, und es wird im allgemeinen angenommen, dass der Abbau von Anstrichfilmen proportional zur Intensität der einfallenden ultravioletten Strahlung vor sich geht.

Untersuchungsergebnisse über die Photo-oxidation des Isopropanols durch TiO<sub>2</sub>, eine Reaktion, die wegen ihrer guten Korrelation mit der Verwitterung von Anstrichmitteln bekannt

ist, deuten daraufhin, dass die Oxidationsgeschwindigkeit bei den normaler Weise vorkommenden Lichtintensitäten proportional zur Quadratwurzel der Lichtintensität ist. Es wird gezeigt, dass diese Schlussfolgerung die Folge der im TiO<sub>2</sub>-Kristall vor sich gehenden Prozesse ist, wenn er durch UV Licht beleuchtet wird.

Die Bedeutung dieser Beobachtungen für die Bewitterungsprüfung von Anstrichmitteln wird besprochen.

## Introduction

Refs. 1-3

In recent years there has been a steady increase in the use of oil based products in the surface coatings industry and the expected decline in available hydrocarbon reserves emphasises the need for coatings with longer service lives. As photo-induced oxidation plays a major role in the outdoor weathering of these materials there is a need to minimise this form of degradation.

The object of research into the fundamental aspects of photo-oxidation is both to improve chalking resistance and to develop better accelerated testing methods. In the former area the value of a better understanding is obvious in that it could lead to significant practical developments. In the latter area, as products improve, development work becomes intolerably slow if only natural weathering results are available, and this underlines the need to place the relationship between natural and accelerated weathering on a satisfactory numerical basis.

\*Paper presented at the Association's Conference held at Stratford upon Avon from 20-23 June 1979.

This paper describes a study of the fundamental processes which occur during the photo-oxidation of  $\text{TiO}_2$  pigmented systems. The photocatalysed oxidation of isopropanol (propan-2-ol) to acetone was chosen as a suitable model reaction since, for a number of commercial pigments, a close similarity between the rates of photo-oxidation of isopropanol and of accelerated weathering of corresponding paint films has been demonstrated<sup>1</sup>. In addition, the mechanism of the reaction has been investigated<sup>2,3</sup>, and it has been shown that sustained isopropanol photo-oxidation, like paint film weathering, requires UV irradiation, oxygen in the gas phase, and water or surface hydroxyl ions.

## Experimental

### Apparatus

Refs. 1,2,4

The reaction was carried out using stirred suspensions of  $\text{TiO}_2$ , typically 0.4 g  $\text{TiO}_2$  in 40 ml isopropanol in an apparatus similar to that already described<sup>1,2</sup>.

UV radiation from Mazda ME/D 250 W medium pressure arc lamps was filtered when required with Ealing Beck interference filters to isolate the 335 nm (Filter Type 26-9068) or 404 nm (Filter Type 31-5853) lines. Chance OXI and OVI filters were superimposed to isolate the 365 nm mercury line. Transmission curves are shown in Figure 1. In some experiments the light intensity was reduced by wire gauze of known transmission. A potassium ferrioxalate actinometer<sup>4</sup> was used to measure the radiation intensity.

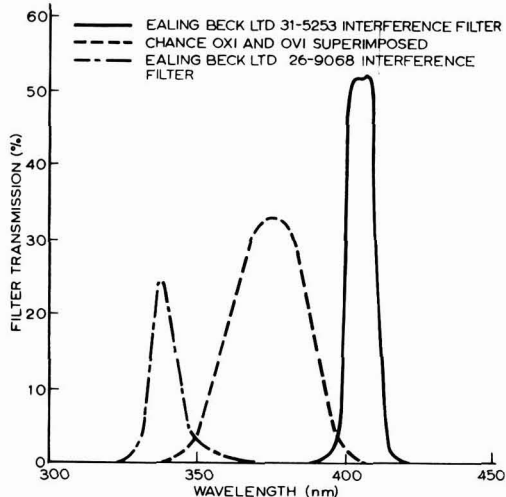


Fig. 1. Filter transmission as a function of wavelength.

Samples of the suspensions were taken by syringe and analysed for acetone content using a Perkin Elmer F17, or Sigma 3, chromatograph with a 1 m, 3 mm internal diameter glass column packed with 15 per cent Carbowax 20M on Chromosorb W at 60°C with  $\text{N}_2$  carrier gas. The instrument was calibrated with synthetic acetone/isopropanol mixtures and straight line calibration curves of peak height vs. acetone concentration were obtained over the range of interest. Their consistency eliminated the need for an internal standard.

## Materials

Ref. 10

Pure rutile (A) was prepared by hydrolysis of  $\text{TiCl}_4$  in solution followed by calcination at 800°C. The surface area measured by a Strohelein single point apparatus<sup>10</sup> was 7.3  $\text{m}^2 \text{g}^{-1}$ . Uncoated pigmentary rutile was prepared by the sulfate (B) or chloride route (C). BDH Analar grade isopropanol was selected with acetone impurity levels of less than 1 ppm.

## Results

### Initial results for pure rutile

Refs. 1-3

Figure 2 shows the effect of light intensity on the rate of isopropanol photo-oxidation by pure rutile at 25°C. The results cover a range of ~300 in light intensity and include experiments carried out with 335, 365 and 404 nm radiation in addition to those with unfiltered UV light. The plot clearly demonstrates that the reaction rate varies as the square root of the incident radiation intensity. The quantum efficiency is low, varying between 0.03 at  $2.1 \times 10^{18}$  quanta/sec and 0.14 at  $10^{17}$  quanta/sec. Photolytic reaction rates depending on the square root of light intensity and of low quantum yield are well known in photochemical studies, and are usually the result of a high bimolecular recombination rate of the species produced in the primary photochemical act.

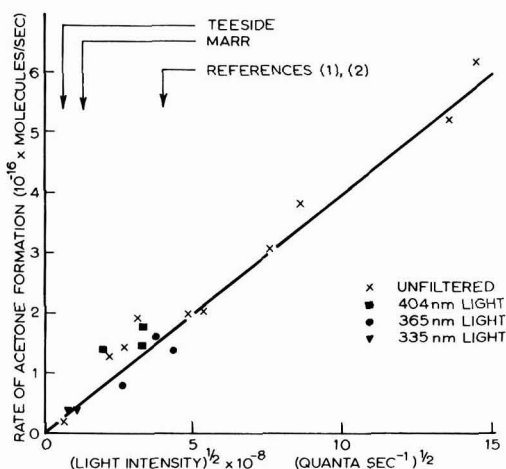


Fig. 2. Effect of light intensity on rate of isopropanol oxidation by pure rutile (Pigment A) showing the dependence of the rate on  $(\text{intensity})^{1/2}$ . Light intensity in various locations and apparatus arrowed.

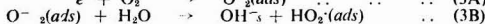
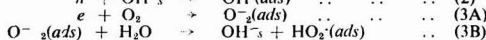
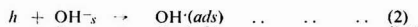
In reactions catalysed by UV irradiated  $\text{TiO}_2$ , the primary photochemical act occurs inside the  $\text{TiO}_2$  crystal. Electrons are excited by the radiation from the valence band to the conduction band, leaving positive vacancies (holes) in the valence band,



Both electrons and holes are free to move about the crystal lattice and in doing so either recombine or reach the surface where they can initiate chemical reactions in the surrounding medium. The relative magnitude of the recombination and surface reaction rate constants then determines the depe-

dence on light intensity of the overall reaction rate, as the following treatment demonstrates.

On reaching the crystal surface, positive holes react with surface hydroxyl groups to form adsorbed hydroxyl radicals, whilst electrons react with adsorbed oxygen to form the  $O_2^-$  radical ion which then attacks a water molecule to form the  $HO_2^-$  radical<sup>1,2</sup>:



Either the hydroxy,  $OH^{\cdot}$ , or perhydroxy,  $HO_2^{\cdot}$ , radical may initiate breakdown of the organic medium, but it is likely that only one of processes (2) and (3) is rate determining. The process involving the other radical completes the reaction and preserves overall charge neutrality. In the treatment that follows, sequence (2) is assumed to be rate determining but this choice does not affect the conclusions since a completely analogous set of equations leads to sequence (3). In the oxidation of isopropanol to acetone, then

$$\text{Rate of acetone formation} = k_3 h = r \quad \dots \quad (4)$$

where  $h$  is the hole concentration, and in the interior of the crystal

$$\text{Rate of hole formation} = k_1 I \quad \dots \quad (5)$$

and

$$\text{Rate of electron-hole recombination} = k_2 h^2 \quad \dots \quad (6)$$

where the simplifying assumption that  $h = e$  is made. More exactly  $k_3^h h = k_3^e e$ , but this does not alter the conclusions.

The steady state concentration of holes may be deduced by balancing their rate of formation against their rate of removal. Thus

$$\frac{dh}{dt} = 0 = k_1 I - k_2 h^2 - k_3 h \quad \dots \quad (7)$$

When  $I$  is large a large number of holes and electrons will be generated hence

$$k_2 h^2 \gg k_3 h$$

$$\therefore k_1 I \approx k_2 h^2$$

$$\text{i.e. } h \approx \left(\frac{k_1 I}{k_2}\right)^{\frac{1}{2}} \quad \dots \quad (8)$$

$$\text{and } r = k_3 h = \left(\frac{k_3^2 k_1}{k_2}\right)^{\frac{1}{2}} I^{\frac{1}{2}} = KI^{\frac{1}{2}} \quad \dots \quad (9)$$

Under conditions of high recombination the rate of oxidation depends on the square root of light intensity—as illustrated in Figure 2. Also since  $k_2 h \gg k_3$  most of the holes recombine with electrons, and  $K$ , the overall quantum yield, is small.

### Results for pure rutile at very low intensities

The converse case to that developed above occurs at very low light intensity when  $h$  must be small. The recombination term  $k_2 h^2$  is then negligible. Hence

$$r = k_3 h = k_1 I \quad \dots \quad (10)$$

i.e. at very low light intensities the photo-oxidation rate should be directly proportional to  $I$ . To test this prediction isopropanol oxidation experiments were extended to very low light intensities. The results are shown in Figure 3 as a log-log plot, and the slope  $S$  of the line indicates the exponent in the  $r = KI^S$  relation. Despite the scatter in experimental results,

a consequence of the very long runs needed to measure low reaction rates, it is clear that at values of  $I$  less than  $5 \times 10^{15}$  quanta/sec the rate of oxidation does vary approximately linearly with UV intensity.

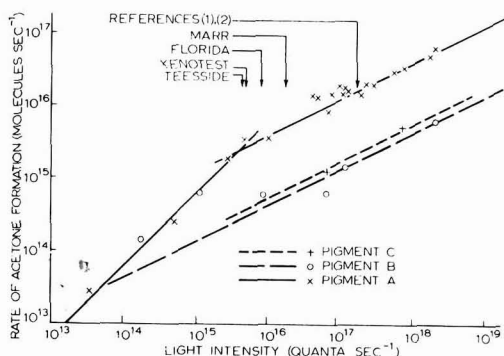


Fig. 3. Effects of light intensity on rate of isopropanol oxidation by pure rutile (Pigment A) and two pigimentary samples (B and C). Light intensity in various locations and apparatus arrowed.

Since there is negligible recombination at these low light intensities, quantum efficiencies should be close to unity. Values in the region of 0.5 to 1.0 were found, greater than those found in the region of high light intensity, 0.03–0.14.

Hence the experiments on pure rutile indicate that the dependence of photo-oxidation on light intensity changes from linear to square root as  $I$  is increased above  $5 \times 10^{15}$  quanta/sec.

### Results for commercial pigments

In view of the unexpected results for pure rutile the experiments were extended to two uncoated pigments. The photocatalytic activity of both these samples is less than that of pure rutile.

It can be seen from Figure 3 that, at light intensities greater than  $5 \times 10^{15}$  quanta/sec, both pigments follow the  $I^{\frac{1}{2}}$  rate dependency. Either a reduction in surface reaction rate,  $k_3$ , or an increase in recombination rate,  $k_2$ , reduces  $(k_3^2/k_2)$  which as shown in equation (9) leads to reduced rate.

Because of the decreased photoactivity the experimental difficulties associated with measurements of acetone formation at low light intensities with pigment B are greatly increased and consequently there is considerable scatter in the results. Despite this scatter it is clear that the acetone formation rate does not vary linearly with  $I$ , unlike the pure rutile case. This may be explained by considering the critical intensity  $I_c$  at which high and low  $I$  approximations are equal. This occurs when

$$k_3 h = k_3 \left(\frac{k_1 I_c}{k_2}\right)^{\frac{1}{2}} = k_1 I_c \quad \dots \quad (11)$$

$$\text{i.e. when } I_c = \left(\frac{k_3^2}{k_2}\right)^{\frac{1}{2}} \frac{1}{k_1} \quad \dots \quad (12)$$

Hence the reduction in  $(k_3^2/k_2)$  responsible for decreased rate also causes the value of  $I_c$  to decrease. In the absence of surface variations, leading to differences in  $k_3$ , the linear rate section should be the same for all pigments.



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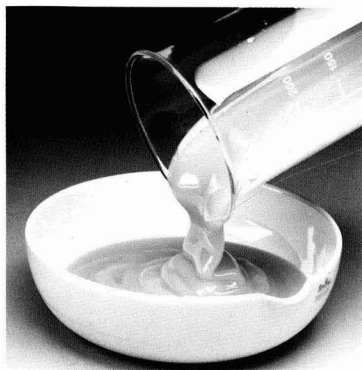
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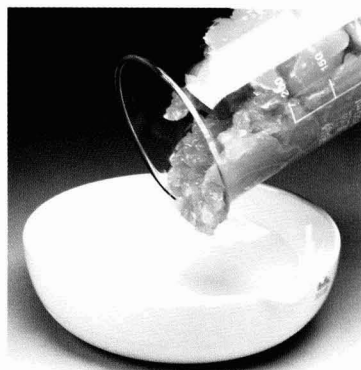
Did you know that TEXAPHOR 963 can also be used as a pre-gelling agent for Bentonite\* gellants? A further interesting field of application for this additive: by contrast with other gels not

containing our product, Bentonite gels with TEXAPHOR 963 have the following advantages:

- softer consistency and thus easier to work into the paint.
- the storage stability of the gel is considerably increased, eliminating crust formation.
- post-addition into the dispersed phase is possible.
- Gels can be produced with TEXAPHOR 963 which are capable of being pumped.
- A synergistic effect occurs between the Bentonites and TEXAPHOR 963.



Bentonite\* gel with TEXAPHOR 963



Bentonite\* gel without TEXAPHOR 963

### Examples using Bentonite and TEXAPHOR 963

- A) Bentonite gel with all-round properties  
 10 parts organophilic Bentonite\*  
 3 parts TEXAPHOR 963  
 87 parts white spirit
- B) Bentonite gel capable of being pumped  
 8 parts organophilic Bentonite\*  
 8 parts TEXAPHOR 963  
 84 parts white spirit
- C) Bentonite gel with maximum thixotropy  
 10 parts organophilic Bentonite\*  
 10 parts TEXAPHOR 963  
 80 parts white spirit

\* = e. g. Bentone 34 or 38. Bentone is a registered trademark of NL Industries Inc, New York, USA.

### Manufacture of Bentonite gels.

The pre-gelling of Bentonite is dependent essentially on the intensity of the stirring and on the length of time which lies between 15 and 20 minutes. Gels containing aromatic solvents should be stirred for 5 to 10 minutes. Bentonite is stirred into the solvent. Using aromatic solvents such as Xylene or Toluene, gelling will have already started at this stage. With the use of white spirit this is not the case. TEXAPHOR 963 is then added and the intensive stirring continues.

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### The influence of wavelength

A feature of the results shown in Figure 2 is that the same straight line can be drawn through experimental points for 335 nm, 365 nm, 404 nm and unfiltered UV light. In the  $I^1$  region there is no evidence of short wavelengths being more effective than longer ones. In the low intensity, linear, region there is less information, but once again there is no strong evidence of wavelength dependent effects. Some results are shown in Table 1.

Table 1  
Quantum efficiencies

$I$ quanta/sec	Wavelength nm	Quantum efficiency
$3 \cdot 10^{15}$	Unfiltered	0.7
$5 \cdot 10^{14}$	335	0.5
$2 \cdot 10^{14}$	404	0.3
$4 \cdot 10^{13}$	Unfiltered	0.8

### The effect of temperature

The effect of changes in temperature from 10–40°C on reaction rate is shown in the form of Arrhenius plots in Figure 4. For pure rutile the measured activation energy is  $\sim 20$  kJ mol<sup>-1</sup>, but for both commercial pigments much higher values,  $\sim 50$  kJ mol<sup>-1</sup>, were obtained

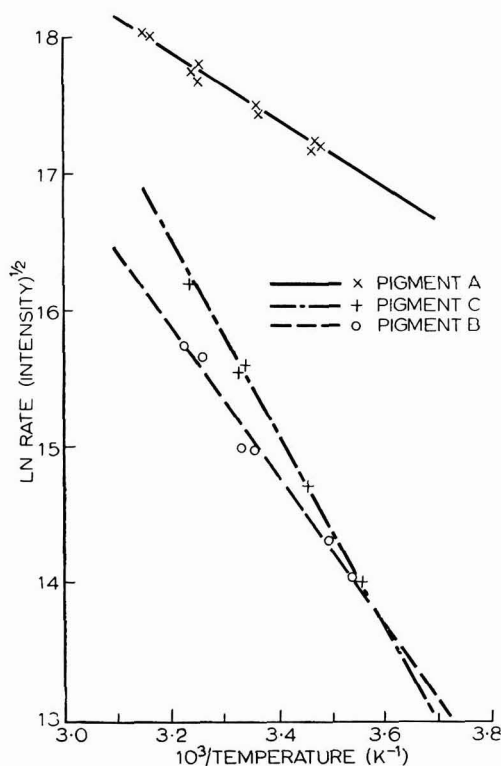


Fig. 4. Effect of temperature on reaction rate.

These measurements were made using unfiltered radiation. Measurements on pigment B using 365 nm light gave an activation energy close to, but marginally greater, than that for unfiltered radiation.

### Discussion

Refs. 1, 5-9

#### Comparison with earlier work

The conclusion that oxidation rate varies as the square root of light intensity appears to be in conflict with the linear dependence reported by Cundall, Rudham and co-workers<sup>1</sup>. The difference between the authors' conclusion and theirs is probably a consequence of the much greater range of light intensities examined in these experiments. In this work  $I$  was varied by many orders of magnitude, in the work of Cundall *et al.* by a factor of 5. Their results may also have been affected by the use of unfiltered UV, as more recent results by Rudham and Ward using 365 nm radiation confirm the square root relation reported here<sup>5</sup>.

The square root dependence is not a result of the detailed chemistry of the isopropanol oxidation reaction; it is instead a general consequence of the mechanism for photoactivity in TiO<sub>2</sub> that has been proposed. The same dependence has also been shown to occur in pigment-catalysed photodecoloration of malachite green and in measurements of photocurrents generated at anodes composed of TiO<sub>2</sub> particles<sup>6</sup>.

#### Implications for accelerated testing

The UV intensity in a twin-arc Marr weathering machine<sup>7</sup> is 40W m<sup>-2</sup> and in a model XW-R Atlas machine 120W m<sup>-2</sup>. Typical UV intensities at outdoor testing stations are 12W m<sup>-2</sup> at Carlton (Teesside) and 20W m<sup>-2</sup> at Florida<sup>8</sup>, assuming that 5 per cent of sunlight is UV. Conversion of these intensities to quanta/sec falling on the same illuminated area as in the present apparatus (2 cm<sup>2</sup>), assuming an average wavelength of 390 nm for a carbon arc and 350 nm for sunlight, gives values in the range  $4 \times 10^{15}$  to  $4 \times 10^{16}$  quanta/sec. Therefore the results described in this paper imply that for commercial titanium dioxide pigments in all practical testing situations the rate of photo-oxidation is proportional not to  $I$  but to  $I^{1/2}$ .

The  $I^{1/2}$  dependence is important for many aspects of durability studies. Thus, in considerations of the effect of wavelength on rutile catalysed photo-oxidation, filters are normally used to isolate selected lines of the radiation source (often a carbon or mercury arc). The different transmissions of the filters when combined with the different intensities of the spectral lines lead to a considerable variation of effective intensity between the lines whose effect is being examined. When comparing the effectiveness of these lines, allowances must be made for intensity differences. Consider two wavelengths 1 and 2, the intensity of 1 relative to 2 being 0.2. Then if 1 and 2 induce photo-oxidation at rates of 6 and 20 respectively an assumption of rate  $\propto I$  leads to the conclusion that 1 is intrinsically more destructive than 2. If, however, rate  $\propto I^{1/2}$  the opposite conclusion results. Figure 3, where results from 335, 365, 404 and unfiltered UV radiation are plotted, suggests that, on a per quantum basis, 335, 365 and 404 nm radiations are equally effective. As the quantum size is inversely proportional to the wavelength, spectral energy distributions should be compared on a quantum rather than on an energy basis.

Table 2

Weathering rates of two paint systems which degrade at the same rate at a standard light intensity  $I_0$ . For system 1 direct oxidation of the organic film is twice as important as the  $\text{TiO}_2$  catalysed breakdown. For system 2 the reverse holds.

Intensity	Wt. Loss of 1 ( $\text{mg m}^{-2}\text{h}^{-1}$ )			Wt. Loss of 2 ( $\text{mg m}^{-2}\text{h}^{-1}$ )			Wt. Loss 1 Wt. Loss 2
	$\text{TiO}_2$ Catalysed	Direct Breakdown	Total	$\text{TiO}_2$ Catalysed	Direct Breakdown	Total	
0.25 $I_0$	1.65	1.68	3.33	3.35	0.83	4.17	0.80
0.5 $I_0$	2.33	3.35	5.68	4.74	1.65	6.39	0.89
1.0 $I_0$	3.30	6.70	10.0	6.7	3.3	10.0	1
2.0 $I_0$	6.67	13.4	18.1	9.48	6.6	16.1	1.12
4.0 $I_0$	6.60	26.8	33.4	13.4	13.2	26.6	1.25

#### Differences between pigment performance at different test locations

At first sight it would appear that a general consequence of the  $I^{\frac{1}{2}}$  dependence would be to reduce differences between various sites. However, it must be remembered that in a pigmented medium the  $\text{TiO}_2$  acts in two ways, one protective, one destructive. It protects the medium by strongly absorbing UV light (and therefore reducing the amount of UV available for direct absorption by the film-forming material) but also acts as a photocatalyst. Hughes<sup>9</sup> has considered this effect and Figures 11–13 of his paper show how the relative magnitude of the two effects can, for example, vary with PVC or type of pigment. In a particular pigmented alkyd film approximately half of the observed weight loss was assigned to direct break-down of the medium by UV, pigment catalysed photo-oxidation accounting for the rest.

Consider the case of two paint systems which at a standard light intensity  $I_0$  breakdown at the same rate. (For ease of calculation the slightly high rate of  $10 \text{ mg/m}^2\text{h}$  is assumed.) For paint system 1 let the direct oxidation of the medium be twice as important as the photocatalysed reaction, for system 2 let the reverse be true. With the assumption that the rate of directly induced oxidation is proportional to  $I$  although the  $\text{TiO}_2$  catalysed oxidation is proportional to  $I^{\frac{1}{2}}$ , the data in Table 2 show the effect of light intensity on the relative performance of the two systems and that even though the two systems behave similarly at an intensity  $I_0$  their relative performance varies as  $I$  changes. At low intensities system 1—in which direct oxidation is important—is more stable. At high intensities the important protective action of the pigment is emphasized.

The direct breakdown of the medium must also be taken into account when considering the effects of both wavelength

#### Discussion at Stratford Conference

MR H. C. A. VAN BEEK asked what was the effect of pigment concentration on the photoactivity, as light absorption would be different at different depths, and this variance would be affected by the pigment concentration. Mr van Beek also asked about the effects of acetone, as this compound causes light-induced oxidation of the solvent.

DR EGERTON stated that work had been undertaken on the effect of pigment concentration. Above a critical value the rate becomes independent of the concentration, i.e. a plateau is reached. All the experiments had been conducted in this plateau region, where all the UV light is absorbed within a short depth, in the film.

The acetone versus time plots obtained had been linear, i.e. no acceleration was observed as a result of acetone for-

and temperature on measured degradation. Even though the authors' results suggest that wavelength-distribution has only minor effects on the  $\text{TiO}_2$ -catalysed reduction it will affect the direct photo-oxidation of the organic medium. For similar reasons the effect of temperature on the relative weathering of systems pigmented with coated or uncoated rutile may not be as large as implied by the activation energies for isopropanol oxidation. Therefore, in the next stage of this work the ideas generated in this study of a model system will be extended to practical paint films.

[Received 5 January 1979]

#### Acknowledgement

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mation. The reason for this was probably because the acetone concentration was always low, rising up to only about 300 ppm in this work.

DR J. C. WEAVER asked whether water had been completely absent from the  $\text{TiO}_2$ /isopropanol suspensions. In about 1931, a practical blue automotive lacquer which showed no weather damage after long exposure on a high mountain (Andes) deteriorated rapidly after being plunged into water in Detroit. This panel could not have been wholly dry, but only devoid of liquid water.

DR EGERTON stated that the reactions were carried out in Analar grade isopropanol. (Traces of water may be present in IPA). No water was added in the experiments, but in work carried out at Nottingham (Refs. 1 and 2), it

was shown that water does increase the rate of reaction.

He suggested that the role of water was presumably to maintain the hydroxylation of the  $\text{TiO}_2$  surface. As shown in the reaction mechanism, the hydroxyl groups are regenerated in this reaction.

DR H. J. LUTHARDT referred to one of the slides which had shown the weight loss plotted against the total exposure, after the system had been pretreated for 140 hours. He asked what sort of pretreatment had been used.

DR EGERTON stated that the pretreatment consisted of exposure in the normal position in the Marr weathering machine. The object of this was to eliminate any anomalous effects which might occur during the first 100 hours of Marr exposure. Thus, the plots presented did not include a contribution from this anomalous region.

MR T. R. BULLETT, referring to Figure 1, asked if an explanation could be given for the fact that the unfiltered UV light was more effective in terms of quantum efficiency than either the 335 or 404 nm light. He appreciated that there were extreme difficulties in measuring quantum efficiency.

He also suggested that the weight loss results obtained in the early stages of artificial weathering might be due to loss of volatiles and water solubles present in the initial dried film. Despite this uncertain factor, he considered the less

than two-fold increase in weight loss with a three-fold increase in intensity for the clear films to be significant.

DR EGERTON said that they would not place too much emphasis on the precise values of quantum efficiency measured in the linear region. What was to be stressed was that the quantum efficiencies in this region are much higher than those measured in the  $\text{H}^+$  region where recombination is dominant.

Dr Egerton stressed that the results given on weight losses had been only from the preliminary investigations, but the clear difference between the behaviour of the pigmented and unpigmented systems was significant. The weight loss change for the unpigmented systems was about two-fold greater.

MR A. G. NORTH asked if the temperature of the film being exposed had an influence on its rate of degradation, and whether any account had been taken of this. In certain accelerated natural weathering services, it was attempted to increase the UV dosage using mirrors, whilst maintaining the temperature by forced convection.

DR EGERTON agreed that different pigments might behave differently with respect to temperature in a weathering situation, and so control of temperature in weathering tests was desirable. The actual activation energies involved were not large, being around 5 kcal/mol for pure rutile (sample A) and 10 kcal/mol for samples B and C.

# Aqueous coil coatings\*

By E. J. Percy and F. Nouwens

Synres International BV, Hoek van Holland, Netherlands.

## Summary

The growth of coil coating processes is described and the relative merits of solvent and water-based systems are discussed. The use of dispersion, colloidal and soluble resins are compared.

Typical paint formulations for water based primers and finishing

## Keywords

*Types and classes of coatings and allied products*

coil coating  
water base paint  
gloss finish  
primer

*Types and classes of structures or surfaces to be coated*

galvanised iron  
aluminium

coats for use in coil coating are given and their final properties on galvanised steel and aluminium substrates are compared.

Durability tests at a number of exposure sites are compared with those obtained by accelerated test methods. The correlation of results was not good.

*Raw materials for coatings*

binders (resins, etc.)  
acrylic resin  
polyester resin  
melamine formaldehyde resin

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

gloss retention  
durability

## Les revêtements pour couchage en continu a base de l'eau

### Résumé

On décrit l'évolution des procédés de couchage en continu et l'on discute les avantages relatifs des systèmes à base et de soljants et de l'eau. On fait une comparaison des aspects de l'utilisation des résines dispersées, colloïdales ou solubles.

On donne des formules typiques pour peintures primaires et pour peintures de finition à base de l'eau et destinées à être utilisées dans le procédé de couchage en continu, et on fait une comparaison

des leurs caractéristiques définitives sur les supports en acier galvanisé et en aluminium.

Les résultats des essais de résistance aux intempéries effectués à plusieurs emplacements sont comparés auprès de ceux qui ont été rendus par les essais accélérés. Dans certains cas la corrélation est satisfaisante, mais la perte de brillant se démontre plus rapide où les panneaux ont été exposés en Floride, Arizona ou Portugal.

## Wässrige Coil-Coating Lacke

### Zusammenfassung

Eine Besprechung der wachsenden Verwendung von Walzenlackierverfahren und der relativen Vorteile von Systemen auf Lösungsmittel- und Wasserbasis. Die Anwendung von Dispersion sowie kolloidal und echt gelösten Harzen wird verglichen.

Typische Lackrezepturen für wässrige Primer und Decklacke für Coil Coatings werden gegeben, ihre Eideigenschaften auf

galvanisierten Stahl und Aluminium verglichen. Die Ergebnisse von Prüfungen einer Anzahl von Bewitterungsstationen werden mit den bei künstlicher Bewitterung erhaltenen verglichen. In einigen Fällen die Korrelation zufriedenstellend, es wurde jedoch gefunden, dass Glanzverlust schneller vorstatten ging, wenn die Bewitterung in Florida, Arizona oder Portugal stattgefunden hatte.

## Introduction

*Refs. 1-4*

The development of coil coating is one of the important and difficult challenges that the coatings industry has had and continues to encounter. The coil coating process itself makes exacting demands on the application properties of the wet paint and on the drying properties. In addition, the coating must survive coiling and uncoiling, and the cutting, forming and assembly of the coated metal—all without losing the appearance and resistance properties needed for such uses as building panels and domestic appliances coatings.

A typical sequence for a coil coating line might be:

Cleaning and pretreatment of coil  
Application of primer and back-coating by reserve roller  
Stoving  
Possibly recoiling and uncoiling  
Application of top coat  
Stoving  
Recoiling

The cured coating might then have to meet the requirements given in Table 1.

Table 1  
*Properties required from coil coatings*

Rheology	—must be suitable for reverse roller application at line speeds of over 100 meter per minute.
Gloss, 60°	—must be constant to $\pm 5\%$ at any chosen value between 10% and 90%.
Hardness	—must be hard enough to prevent blocking, metal marking or damage during recoiling, forming and handling.
Flexibility and adhesion	—No cracking or loss of adhesion during forming.
Durability	—must retain its decorative appearance without corrosion, discolouration, chalking etc. under service conditions.

The growth and size of the coil coating industry means that the challenge is being met with some success. The United Kingdom production of coated coil has grown from 49,000 tons in 1969 to 104,000 tons in 1976, with over 200,000 tons being predicted<sup>1</sup> for 1984.

The total production of precoated metal coil by North

\*Paper presented at the Association's Conference held at Stratford upon Avon from 20-23 June 1979.



American coaters is given<sup>2</sup> in Table 2 in millions of pounds weight.

Table 2

year	aluminium	steel
1962	343	585
1966	593	1,650
1970	1,100	2,274
1974	1,414	4,174

The National Coil Coaters Association have published figures for the American supplies of coated coil in 1975 to the various user industries, as shown<sup>3</sup> in Table 3.

Table 3

Industry	Aluminium	Steel
Building products	293,960 tons	611,138 tons
Transportation	20,104	199,809
Appliances	5,781	81,857
Containers	127,932	62,612
Furniture	1,243	63,178
Other	19,933	124,352
Total	466,953	1,142,946

What are the factors encouraging this growth?

Initially, economics was the driving force. It is cheaper and more efficient to pre-coat large areas of sheet metal in a coil coating line than first to cut and form components individually, and then to clean, pretreat and paint them.

Consistent quality and quality control were factors which also encouraged the development of coil coating in the early years. As the coatings technology developed and a wider range of coated coil became available, more industries adopted the use of pre-coated metal as an alternative to applying paint themselves. More recently, environmental factors have become even more important. It is easier to cope with pollution abatement problems at one large, coil coating plant than at a large number of smaller paint lines spread throughout the country.

Pollution by vapour emission from organic solvent based coatings can be controlled by incineration, and the heat generated from burning the organic solvents can be used to heat the oven air. A practical alternative is to use water-borne coil coatings, and a number of coating lines are now doing this very successfully.

Powder coating is another alternative, but this is limited by the range of resins currently available. Radiation-curing coatings have also been tried, but again a limiting factor is the difficulty of finding a coating formulation which satisfies all the requirements mentioned previously. A further difficulty is that ultraviolet radiation will not cure thick, pigmented coatings, so it is necessary to use electron beam or more penetrating radiations.

Electrodeposition is another possibility, but as with powder coating and radiation curing, it would require major plant changes in any established coil coating line. The changes necessary to convert to water-borne or high solids coatings have proved to be much less extensive.

It is possible that several of these alternatives will be used in the future, but water-borne systems are sure to play an

important role. What are the main advantages of using water as a solvent?

Water is non-flammable, non-toxic, non-polluting and not expensive. Water-based systems reduce effluent problems and explosion hazards, and improve working conditions in general. Energy savings can also be made in many instances. For example, less hot air is required in the ovens to keep below the explosion limit because there are less organic vapours to dilute<sup>4</sup> (Table 4).

Table 4  
Emissions during stoving

Coating system	Organic solvents	Reaction products
Solvent-based alkyd-amino coating 48% solids	70	3
High solids alkyd-amino coating 80% solids	16	3
Water-borne acrylic-melamine coating 60% solids	7.7	1.3
Acrylic-isocyanate powder coating 100% solids	0	5.4

Figures are kilogram of vapour per 1,000 m<sup>2</sup> painted metal at 25 microns dry thickness.

The cost of water compared with the price of organic solvents will be even more important in the future.

Of course, there are also disadvantages in the use of water, such as:

- It has a high surface tension which reduces surface wetting properties of the paint
- It has a high heat of vaporisation
- Large changes in the humidity of the air affect drying rates
- Water has a high freezing point
- It can cause rusting
- It encourages the growth of micro-organism in the paint
- Clean-up is usually more difficult with water-borne paints
- Water-borne systems have a greater tendency to foam

All of these difficulties have been overcome, but some of the cures may cause other problems. For example, the addition of glycols improves wetting and drying, but increases pollution problems.

The major motivation for changing to water-borne systems is currently the need to control airborne emissions from ovens more effectively. In the future, the main reason for change may be the high cost of solvents.

### Water-borne resin systems

Water-borne resins may be conveniently classified into three overlapping groups on a physico-chemical basis, i.e. aqueous dispersions (or emulsions) colloidal or water "solubilised" dispersions, and water solutions. Their principal characteristics may be summarised as shown in Tables 5 and 6.

These characteristics affect the paint-making and paint-application properties and also the coating performance properties.

In practice, all three types of water-borne polymers are used in coil coating formulations, and usually more than one



Table 5

Property	Dispersion Resins	Colloidal Resins	Soluble Resins
Particle size	over 0.1 micron	typically 0.02-01 micron	non-particulate
Typical molecular weight	500,000	100,000	30,000
Viscosity	low and independent of molecular weight	intermediate	high and very dependent on molecular weight

Table 6

Property	Dispersion Resin	Colloidal Resin	Soluble Resin
Pigmentation	difficult	intermediate	easy
Solid-content at application viscosity	high	intermediate	low
Flow levelling and gloss	poor	intermediate	good
Durability and resistance	good	intermediate	fair

type will appear in the same formulation. A water-soluble component is used to improve gloss, pigment wetting and roller coating properties, and a dispersion component is used to increase application solids content, toughness, exterior durability and resistance properties. Colloidal dispersions can be considered as hybrids of the other two types.

Water-borne resins can also be classified according to their chemical type. At the present time, the most successful water-borne coatings for coil coating are based on polyester or acrylic resins. Both types are normally cross-linked with a water-soluble melamine resin during stoving, so the final film is very complex chemically.

Both the polyester and the acrylic resins are sometimes chemically modified with a silicone. This increases the cost but can greatly extend the resistance to outdoor exposure.

A typical polyester might be made from a mixture of adipic acid, isophthalic acid and trimellitic anhydride, esterified with an excess of polyols such as pentaerythritol, trimethylolpropane, neopentyl glycol or glycerol. The amount of chain branching and the molecular weight of the polyester, together with the cross-link density of the cured film, control the performance properties of the coating, e.g. flexibility, hardness, resistance.

The structure of the acrylic types similarly affects coating performance. Table 7 shows some commonly used monomers and indicates their influence on film properties.

Table 7

Monomer	Film Property
Methyl methacrylate	exterior durability hardness stain and water resistance
Styrene	cost reduction hardness
Butyl and higher acrylates	flexibility water resistance
Hydroxy(meth) acrylates	functional groups for cross-linking
Acrylic and methacrylic acids	functional groups hardness

### Paint formulation

The formulation of the paint is just as important as the type and quality of the resin, so a typical formulation will now be

discussed in order to illustrate the formulating process.

Firstly the resin and cross-linking system must be chosen. Whether this is a polyester or acrylic dispersion, it is preferred to use as cross-linker a water-soluble hexamethoxymethyl melamine (HMMM) because it has a high solids content, gives a very low level of formaldehyde emission during stoving, and it gives a suitable cross-linking pattern during curing. For the hydroxyacrylic resin the optimum ratio of resin: HMMM lies between 90:10 and 70:30. Next the pigments must be chosen. This is crucial because pigments can have unexpected effects on properties. For example, it was found that the curing was affected by a particular grade of titanium dioxide. Pigments, are chosen initially on the basis of colour, hiding power, durability, and their suitability for aqueous systems, but they also have to be checked carefully in every formulation.

The HMMM is used as the grinding medium but the pigment wetting can be improved by lowering the surface tension by adding a little dimethylethanolamine (DMEA).

If the surface tension is lowered too much, foaming problems arise, so it is important to strike the right balance. The volatile DMEA will evaporate from the coating in the first part of the oven and so will not inhibit curing properties.

HMMM is not completely water dilutable and so a little solvent is included in the mill base to help prevent flocculation when the mill base is mixed with the acrylic resin dispersion. This solvent also assists the coalescing agents to improve film formation, and optimum results were obtained from the combination of solvents given in Table 8.

The polypropylene glycol also acts as a coalescing agent, but this will not evaporate from the film during stoving. It will become cross-linked into the coating and will act as an internal plasticiser and increase the flexibility.

If the gloss must be lowered, a flattening agent such as amorphous silica is added. This may decrease the resistance to metal marking and so to overcome this problem, a little polyethylene wax is used.

This leads to the formulation given in Table 8.

### Application Properties

It is expensive to experiment on a coil coating line, so the initial tests of application properties are made on a laboratory

machine, such as the Giordano applicator. This simulates the reverse roller applicator quite well, and allows formulations to be screened or adjusted before they are tried on the coating line.

Table 8  
White coating formulation for coil

		weight %
Hexamethoxymethylmelamine, 98%	(1)	3.8
Coalescing agent	(2)	1.1
Water		0.6
Solvent 1	(3)	5.4
Amine	(4)	0.3
Rutile titanium dioxide	(5)	30.4
	Mill base	41.6
Acrylic dispersion, 50% solids	(6)	53.2
Polypropylene glycol	(7)	1.1
Polyethylene Wax dispersion	(8)	3.4
Solvent 2	(9)	0.7
		100.0

- (1) Cymel 303, Cyanamid
- (2) Butyl Carbitol, Union Carbide
- (3) Butyl Glycol
- (4) Dimethylethanolamine
- (5) Tioxide R-CR2, Tioxide International
- (6) Synres
- (7) Molecular Weight approx. 1200
- (8) Hardamer PEO2, Hoechst
- (9) Ethylene Glycol

Density, Kg/m <sup>3</sup>	1320
Solids content, weight %	63
Solids content, volume %	51
Pigment Volume concentration, %	20
Application viscosity, DIN, 4 mm, 25°C	32 secs.
Thinner	tap water
Oven temperature	260°C
Peak metal temperature	230°C
ASTM D2243 Freeze-Thaw stability	over 7 cycles

The rheology of water-borne dispersions is not the same as that of conventional coil coatings based on organic solvents. The aqueous systems are generally applied at lower viscosities than the organic solvent systems, and the optimum viscosity is dependent upon the line speed. The faster the line speed, the higher the viscosity.

The speeds of the pick-up and application rollers have to be changed for water-borne systems, e.g.

	Organic-solvent system	Water-borne system
Line speed	70 m/min.	70 m/min.
Pick-up roller	60 m/min.	40 m/min.
Application roller	80 m/min.	110 m/min.

Harder rollers may have to be used at the higher speeds.

The pick-up roller should be as deep as possible in the paint to prevent the paint from slinging off the roller and causing starve-out effects on the coil.

The paint circulation rate should be higher for water-borne systems because of their tendency to dry-out faster. This fast circulation encourages foam formation and the design of the recirculation system may have to be adjusted. Sharp corners should be avoided and the paint should not be allowed to splash or fall freely. Overflow weirs, return hoses, and filtration have all been used to prevent foaming.

If the paint pans, etc. are not made of stainless steel, it may be necessary to use a little rust inhibitor in the paint.

It is important to keep the coater clean and to prevent the paint from setting. Once set, the dried coating will not dissolve in the wet paint again so it is essential to stop dry particles coming back into the wet paint system via the reverse roller.

The drying characteristics of water-borne systems require changes to be made in the stoving schedule. The temperature in the first zone of the oven may be reduced by about 100°C to allow a longer flash-off time and better levelling. The cross-linking can be carried out easily in the following sections of the ovens because a relatively low peak metal temperature (PMT) is required for full curing. After stoving at a PMT of 230°C, the water-borne coating had the properties given in Table 9.

### Durability testing

Most coil-coatings must have a long life and the most widely

Table 9  
Properties of water-borne acrylic coating

The top coat formulation is given in Table 8, and the primer formulation in Table 10.

Substrate Pretreatment Primer		Aluminium Bonder 722 None	Galvanised Steel Bonder 1303 Water-borne acrylic
ECCA-T-1	Dry film thickness	23 micron	32 micron total
ECCA-T-2	Specular gloss, 60°	89%	80%
	Specular gloss, 20°	72%	53%
ECCA-T-4	Pencil hardness	F	F
ECCA-T-5	Reverse impact	45 inch·lb	<7 inch·lb*
ECCA-T-6	Adhesion after Erichson	95%	55%*
	Adhesion after impact	95%	35%*
ECCA-T-7	Bendability	T ½	T 5*
ECCA-T-8	Salt spray resistance after 500 hours	<2 mm	<2 mm
ECCA-T-9	500 hours water immersion	no effect	no effect
ECCA-T-11	Metal marking	8	8
ECCA-T-12	Buchholz indentation	118	67
ECCA-T-13	Bendability after 5 minutes at 140°C	T = 1	T > 5*

\*The zinc layer cracks and loses adhesion during these tests.

accepted test for exterior durability is the Florida exposure test. However, it is essential to use accelerated ageing tests in order to develop new systems at a reasonable rate.

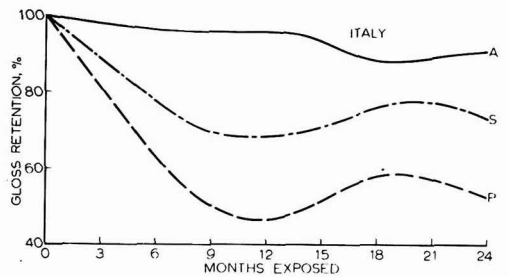
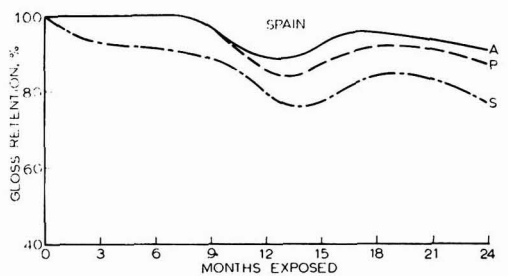
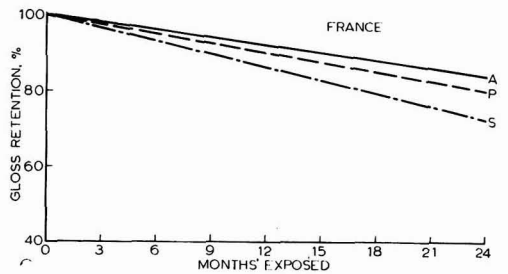
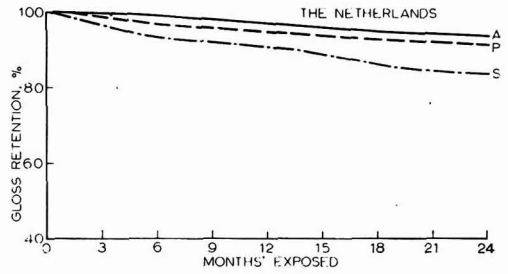
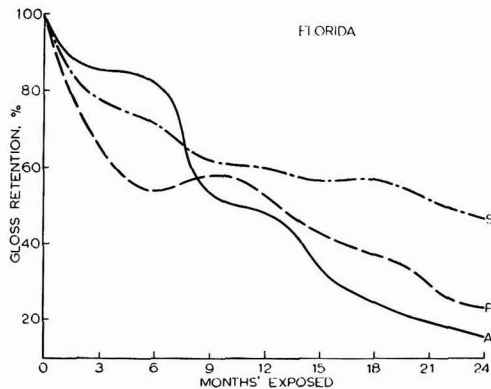
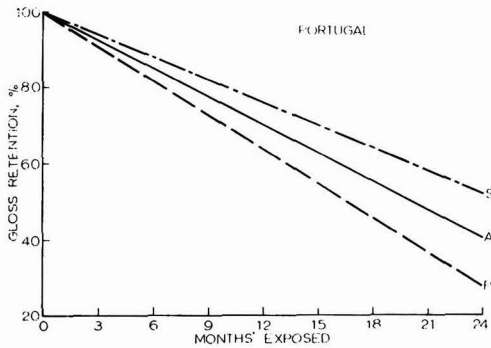
Table 10  
Formulation for water-borne acrylic primer

		Weight %
Methylated melamine	(1)	10.0
Propylene glycol		2.0
DMEA		0.5
Rutile titanium dioxide	(2)	7.5
Strontium chromate	(3)	4.0
Mill Base		24.0
Acrylic copolymer dispersion, 50%	(4)	76.0
		100.0

- (1) Cymel 370, Cyanamid
- (2) Tioxide R-CR2, Tioxide International
- (3) Type SY 70, Remmert
- (4) Synres

The authors have tested coatings by a number of well-known exterior exposure tests and laboratory accelerated ageing tests, but find it difficult to correlate the results.

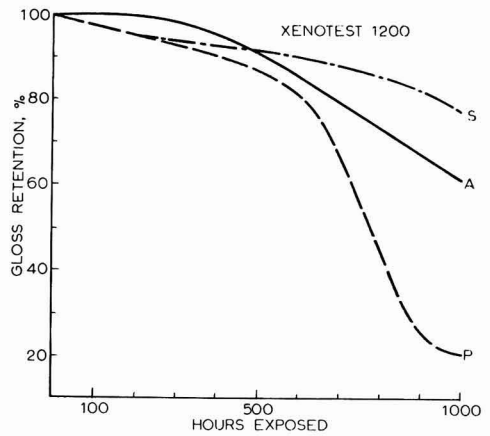
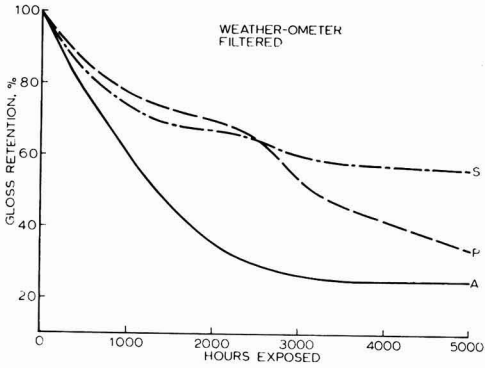
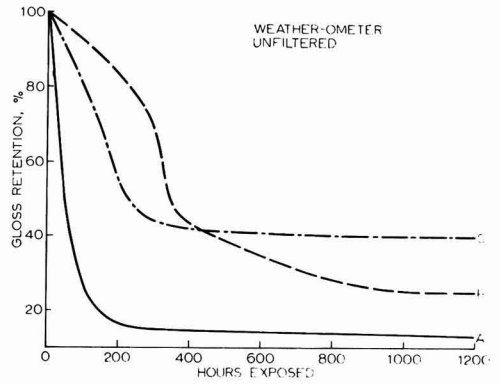
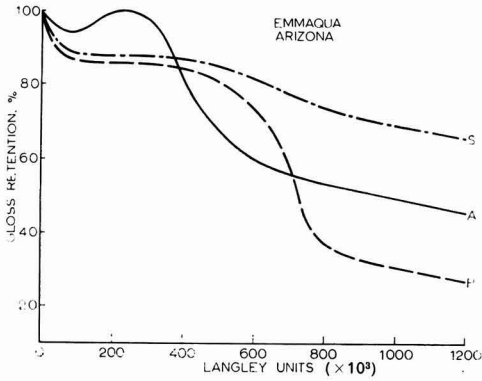
Some results are shown in the following graphs. A, P, and S are three coatings based on acrylic, polyester and silicone-modified resins. All three were tested together under identical conditions in each of the various tests. Each coating was tested in duplicate, and the agreement between the duplicates was excellent.



Identical panels coated with A, P or S were exposed at the following Synres sites facing south at an angle of 45° to the vertical direction:

- Hoek van Holland, Holland (coastal)
- Compiegne, France (rural, inland)
- Filago, Italy (Po valley, inland)
- Lisbon, Portugal (industrial, coastal)
- Viladecans, Spain (urban, coastal)
- Mexico City (industrial, high altitude)

Identical panels were also evaluated independently for exterior exposure resistance in Florida and Arizona (Emmaqua), and accelerated ageing tests were carried out on identical coating formulations in Dutch laboratories using the Weather-Ometer, QUV, and Xenotest 1200 equipment.



From the graphs, it is clear that the results of these tests are not in agreement. There is a good correlation between the results of the exterior exposures in Holland, France and Spain, where the gloss retention was good over the two year period. Different results were found after two years in Florida, Arizona and Portugal, where the gloss decreased

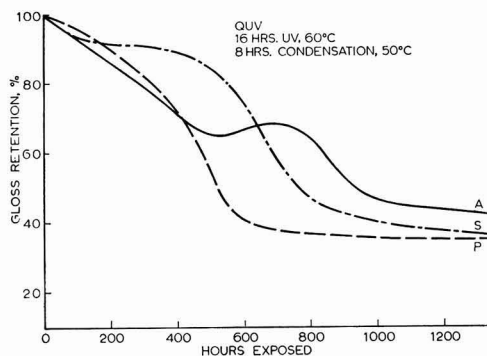
much faster. Perhaps these two sets of results should be compared on different time scales.

Table 11

Substrate	Aluminium	Aluminium	Galvanised Steel	Galvanised Steel
Pretreatment	Bonderite 722	722	1303	1303
Primer	—	—	WB <sup>1</sup>	epoxy <sup>2</sup>
Curing primer	~260°C	—	55"	55"
PMT °C	—	—	199	199
Dry film thickness μm	—	—	6	8
Finish	WB-A	Pol.	WB-A	Pol.
Curing finish	65"	75"	90"	110"
PMT °C	232	241	232	241
T 1 dry film thickness μm (total)	23	22	32	30
T 2 Gloss 20°	72%	66%	53%	43%
60°	89%	92%	80%	82%
T 4 Pencil hardness	F	H	F	3H
T 5 Impact reverse in-lb	45	35	> 1	< 1
T 6 Adhesion after 5 mm Erichsen	95%	50%	55%*	20%*
Adhesion after 40 in-lb reverse impact	95%	40%	35%*	20%*
T 7 Bendability, T value	1/2	1.5	5*	> 12 < 15*
T 8 Salt spray test, 500 hrs.	< 2 mm	< 2 mm	< 2 mm	< 2 mm
T 9 Water immersion test, 500 hrs.	no effect	no effect	no effect	no effect
T11 Metal marking	8	9	8	8
T12 Buchholz indentation, E-value	118	85	67	67
T13 Heat resistance, 5'-140°C, T-value	1	3	> 5*	> 15 < 20*

\*The zinc layer cracks and loses cohesion as soon as the metal is deformed.

- (1) water-borne primer formula, Table 10.
- (2) epoxy primer formula, Table 12.



The curves obtained from the Weather-Ometer (filtered) tests are very approximately the same shape as the Florida curves, but the gloss reduction of *A* relative to *P* is greatly accelerated. The unfiltered Weather-Ometer tests results emphasize this effect. The QUV and Xenotest results are also difficult to correlate with the exterior exposure results. Obviously, it must be concluded that accelerated weathering tests give only an approximate indication of exterior durability, and the results of accelerated tests must be used very cautiously.

### Conclusions

Water-borne coil-coatings will grow even faster than solvent-based coil-coatings, and water-based systems are now available which give equivalent or better properties than solvent systems (Table 11).

Some equipment changes are needed to change a line from solvent to water-based products, but these changes are insignificant compared with some other "environmentally

### Discussion at Stratford Conference

DR J. E. O. MAYNE referred to the graphs showing the loss of gloss of duplicate panels upon exposure at six exposure stations. At four of them the gloss steadily declined, but at two, Spain and Italy, after a slight initial decline the gloss increased. He asked if the authors could offer any explanation for this behaviour.

Dr Mayne pointed out that the main factors controlling the degradation of paint films were water, atmospheric pollutants, such as sulfur dioxide, and radiation, either infrared or ultraviolet. Since the degradation takes place by at least two different mechanisms, oxidation and depolymerisation, he suggested that if records were available of the temperature, pollution, hours of sunshine and rainfall at each exposure station, then a statistical analysis might yield information regarding the factors which controlled the rate of degradation of the paints.

On the first point, MR NOUWENS said that the exposure tests had commenced in the late autumn, and he pointed out that the graphs indicated gloss retention, and did not start at 100 per cent gloss, but at an initial reading which was taken as 100 per cent retention. If a particular panel started with say 50 per cent actual gloss, then during the winter when the panel would be exposed to large amounts of rain and only a little sunshine, then the surface might become smoothed down, thus increasing the gloss.

Table 12

Epoxy primer		weight %
Plasticised epoxy resin	(1)	61
Titanium dioxide	(2)	6
Strontium chromate	(3)	4
Talc	(4)	3
Solvesso 150	(5)	12
Solvesso 100	(5)	10
Butyl carbitol	(6)	4
		100
appl. viscosity DIN Ø 4		65"
density kg/m <sup>3</sup>		109 <sup>11</sup>
solids by weight %		40
solids by volume %		31
PVC		13

- (1) e.g. Eporex AP2245 ex Synres NL
- (2) e.g. Tioxide R-CR2 ex Synres NL
- (3) e.g. type SY70 ex Remmert NL
- (4) e.g. Micro talc AT I ex Norwegian Talc, Norway
- (5) ex Exxon U.S.A.
- (6) ex Union Carbide U.S.A.

acceptable" systems, such as powder coating or electro-deposition.

Some coil-coaters have adapted their heating burners in order to use the solvent vapour effluent arising from solvent-based coatings, but many coil-coaters intend to meet the challenge of new pollution legislation, energy and cost saving by the use of water-borne coatings.

[Received 27 March 1979]

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2. *Products Finishing*, 1974, 38, July, 75.
3. *Products Finishing*, 1976, 40, July, 70.
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He stated that some information was available on the climatic conditions at the test sites during the exposure periods, but he thought that they would be insufficiently detailed to perform any valid statistical analysis.

DR B. ANDERSSON reported that, in Sweden, they had been using water borne (latex) formulations for about 20 years for coil coating and in building applications, based originally on polyvinyl acetate, but for the last 10 years based on acrylic formulations. They had not been confident using acrylic latex formulations as primers as these had regularly given poor outdoor durability and salt spray resistance. If epoxy based products or solvents are not acceptable, then water soluble formulations based on urethane modified products, with acrylic top coats may be used. He asked if the authors had an acrylic latex primer which gave good exterior durability and salt spray resistance on galvanised steel.

Dr Andersson also queried the T-bend values given in Table 11 which ranged from 10 to 25 on galvanised steel and 1 to 3 on aluminium. He asked if this was considered acceptable, as in Sweden they used values T0-1.

MR NOUWENS said that when a water-borne top coat was used, and if an epoxy based primer was used, then an afterburner was still necessary to avoid the emission of

solvents into the atmosphere, so that when the new machinery is installed, the manufacturer who wishes to avoid using an afterburner will still use a water based primer. Although the water based primer does not give as good durability as does a solvent based system, it will often be used for this reason. The biggest problem with the water based primer is the salt spray resistance, which is a result of the completely different system, but in outdoor exposure tests in Florida, these systems had been exposed for up to two years without any noticeable differences. However, recent publications have indicated that isocyanate curing systems fail after about seven years, and so they are not able, as yet, to give a guarantee for twenty years, as most users require, on the basis of only two years exposure.

Dr Andersson indicated that it was possible to make formulations based on water soluble polyurethanes which, in their experience, performed better as primers than the acrylic based latex formulations.

Mr Nouwens indicated that they had examined some of these systems which were commercially available, but they had found that the major differences were caused by the amount of care taken in pretreatment, rather than the type of primer used.

Referring to the high T-bend figures, Mr Nouwens explained that, these were obtained using a microscope which revealed cracking on galvanised steel, and it had been decided, to be realistic, that these figures obtained with the microscope should be published.

DR M. L. ELLINGER asked if the acrylic dispersions used had been of the thermoplastic or thermosetting type.

MR NOUWENS said that the inside of the particles were thermoplastic, and only the reactive parts on the surface of the particles were used, because with the short time in the oven there is almost no flow of the HMMM across the whole particle, and so it is useful to have the reactive group only on the surface.

DR M. L. ELLINGER asked if the acrylic dispersions chalking, there had been a more marked effect with the QUV exposure tests than with the other accelerated test methods. She pointed out that in the graphs showing the Emmaqua test results, gloss retention was related to Langley's received, whilst in all other graphs it was related to the duration of exposure. Correlation of the results is, nevertheless, possible, because at the Arizona site where Emmaqua machines are operated, the amount of irradiation is measured every day and the data recorded in Langley units are published monthly.

Referring to Dr Mayne's question on the recording of climatic conditions at the outdoor exposure sites, Dr Ellinger informed the delegates that at all established "weathering stations", such as those in Arizona or Florida and at many in Europe, the climatic data are regularly recorded and are available, thus enabling a statistical analysis to be performed.

Mr Nouwens agreed that the chalking results from the QUV exposure tests had been much more rapid and severe than with the other methods, and they had also noticed large differences in results obtained with titanium dioxide from the sulfate and chloride processes in water-borne acrylic systems. Titanium dioxide from the chloride process had been chosen for use in the exposure tests, but this problem had been encountered and they had changed to

using sulfate process pigments, which showed much less chalking with water-borne systems. Mr Nouwens stated that the climatic recordings were indeed available for the Florida exposure and some others, but not for exposure in Portugal, etc.

MR J. M. RACKHAM stated that in Tioxide's work on water-borne industrial finishes, many of their ideas on TiO<sub>2</sub> selection formed from working with non-aqueous paints had been revised because it was found impossible to predict whether TiO<sub>2</sub> pigment dispersion stability would be satisfactory on the basis of resin composition. Some very unusual pigment-resin interactions had been found. Flocculation was invariably the reason and, therefore, all paints were checked for degree of flocculation. No bias towards sulfate or chloride route TiO<sub>2</sub> had been found.

Mr Rackham suggested that sometimes the poor performance of some of the systems mentioned in the paper might be due to excessive flocculation, so giving inferior gloss results and poorer film integrity than might be expected from the resin used.

Mr Rackham pointed out that an examination of the gloss results for the silicone modified products at the various exposure sites, always seemed to yield a similar final figure. He asked if the authors would like to comment on this.

MR NOUWENS explained that the siliconised product had a tendency to pick up dirt on the surface, which was not cleaned, so giving a rapid initial drop in gloss, but thereafter a more constant figure.

MR E. V. COLLINS commented that from the paper it seemed that strontium chromate had been used as the anticorrosive primer pigment, and for toxicological and environmental reasons this was not a normal choice. He asked what alternatives there were and how critical was this selection.

MR NOUWENS said that many pigments had been tried, and it was always preferable to use the least toxic pigment, and it had been general policy to use as much as possible of a pigment, such as zinc phosphate, but it appeared that for water-borne systems the only suitable anticorrosive pigment to provide an acceptable salt spray resistance was the one which had been used.

MR C. P. RYCROFT asked about the relative costs of the water-borne system as opposed to the solvent based systems, bearing in mind that the relatively high energy of vaporisation of the water-borne system would entail an increased energy input or a reduction in the line speed.

MR NOUWENS pointed out that the amount of heated air needed in the oven was much reduced as there was no need to remove large quantities of volatiles from the atmosphere. Also, as the system used was rather reactive, it was possible to reduce the peak metal temperatures. In his tests, with a three stage system, the temperature of the first oven was reduced to about 160°C and the final two left as normal. The line speed was then increased to avoid breaking down the acrylic, which is sensitive to high temperatures.

DR PERCY added that a large amount of the energy went towards heating the metal, which would be the same for both types of system.

MR S. VOUT asked the opinion of the authors on whether the future of water based coil coating involved using disper-

sions or water soluble polyester types, and also what film thickness had been used with the dispersion types.

MR NOUWENS said that a film thickness of between 20 and 25 microns had been chosen for the finish and about 6

or 7 micron for the primer system. He considered that in the near future the emphasis would be on emulsion or dispersion types which do not contain any organic solvents. Perhaps water soluble polyesters would be used if a system was found which gave equivalent water resistance after curing.



# Dispersion of pigments: What is the ultimate?\*

By D. M. Varley and H. H. Bower

Ciba-Geigy Plastics & Additives Co., Pigments Division, Roundthorn Estate, Wythenshawe, Manchester M23 9ND

## Summary

Much has been published regarding the degree of dispersion of pigments and how increasing dispersion results in better performance, but it still remains a fact that in many cases pigment users do not obtain the best possible value from the pigments they use.

Some of the properties of pigmented systems which can be improved by better dispersion are discussed. It is possible for either the pigment manufacturer or its user to be the controlling factor in

determining the level of dispersion obtained.

The areas in which the pigment user can improve his efficiency are identified and the potential advantages to be gained by using more specific dispersions are discussed, particularly with reference to non-aqueous paints. General purpose stainers are considered in comparison with specially developed products for individual applications.

## Keywords

*Processes and methods primarily associated with manufacturing or synthesis*

pigment dispersion  
flocculation

*Raw materials for coatings  
prime pigments and dyes*

tinting colour  
organic pigment

*Properties, characteristics and conditions primarily associated with materials in general*

opacity

*raw materials for coatings and allied products*

tinting strength

*Miscellaneous terms*

cost

## L'état de dispersion de pigments-Quel est l'ultime ?

### Résumé

Bien des exposés ont été publiés au sujet de l'état de dispersion de pigments et de la manière par laquelle son augmentation peut assurer un meilleur rendement, pourtant il reste encore indiscutable qu'en plusieurs cas les usagers de pigments n'obtiennent pas la meilleure valeur possible à partir des pigments qu'ils utilisent.

On discute certaines propriétés des systèmes pigmentés qui peuvent être améliorées au moyen d'un meilleur état de dispersion. Il est possible que soit le fabricant de pigments soit l'utilisateur exerce

l'influence prédominante sur la détermination du niveau de dispersion obtenu.

On identifie les domaines où l'utilisateur de pigments peut améliorer l'efficacité de ses procédés, et on discute les avantages éventuels offerts par l'utilisation des dispersions plus spécifiques, surtout à l'égard des peintures non aqueuses. On considère les teintes-mères polyvalentes en comparaison auprès des produits spécialement conçus pour les applications particulières.

## Dispergierung von Pigmenten-Welche Methode ist die allerbeste ?

### Zusammenfassung

Über den Feinheitsgrad von Pigmentdispersionen und wie stark verbesserte Dispergierung die Qualität verbessert, ist schon viel veröffentlicht worden. In vielen Fällen erzielt jedoch der Pigmenthersteller noch immer nicht das best mögliche Ergebnis.

Es werden einige der Eigenschaften pigmentierter Systeme, besprochen welche durch bessere Dispersion verbessert werden können. Sowohl der Pigmenthersteller als auch der Verarbeiter können den Dispersionsgrad kontrollieren.

Die Gebiete, auf welchen der Pigmentverarbeiter seine Resultate verbessern kann, werden aufgezeigt, und die durch Benutzung spezifischer Dispergierungsmethoden möglichen Vorteile, insbesondere mit Bezugnahme auf nicht-wässrige Anstrichmittel, werden besprochen. Allgemein gebräuchliche Anfärbepasten werden in Betracht gezogen im Vergleich mit speziell entwickelten Produkten für individuelle Anwendungen.

### Introduction

One of the most dominant and recurrent problems in the world today is that of economy. In the paint industry, the demand for improved surface coatings is always tempered by factors of cost. In selection of pigments, the inflationary state of the industry as a whole poses many problems.

Many factors are outside the immediate area of control, e.g. raw materials, overheads, services, labour etc., but if the factory operation is considered a little more closely, is it possible to increase efficiency and productivity by using the existing resources better? What advantages can be gained by modifying procedures?

It is this latter question which can now be taken a little further, looking at some of the factors involved, suggesting not only how the paint maker can help, but also how the pigment manufacturer, with his specialised knowledge of pigments, can provide many of the answers by utilising his more specialised products.

### Requirements of a pigment

From a users point of view a pigment should give maximum colour strength per unit cost, require minimum energy input to achieve dispersion, give the best colouristic effect, and give an acceptable balance of fastness properties.

Coloured pigments are a very expensive part of any paint

\*Paper presented at the Association's Conference held at Stratford upon Avon from 20-23 June 1979.

formulation and the correct selection to give the best value is very dependent on their being used properly. As well as choice of pigment, the method used to disperse it is important, but the detail of this can be left to the equipment maker. The point must be made that an alternative physical form can be more economical in overall consideration, even though it does not make full use of all existing equipment.

### Effect of dispersion

Refs. 1-4

Efficient use of a pigment is largely dependent on the level of dispersion attained. Improvements in dispersion affect various properties, some to the good, others adversely. For example, likely improvements are in colour strength, brightness (and possibly a change in hue as well), gloss and gloss retention, transparency, flocculation resistance and dispersion stability, but decreases are likely in opacity, weathering and lightfastness, and flow (but dependent on overall stability).

These changes vary from pigment to pigment and the overall effect on economy can be considered only in terms of individual requirements.

In assessing levels of dispersion, it is necessary to consider the particle size distribution, not some odd particles, and to look at the sub-micron range. A Hegman Gauge reading of 7 or 7-8 (10-15 $\mu$ ) is not very meaningful<sup>1</sup>.

### Effect on strength

The Mie theory<sup>2</sup> suggests that with transparent, high strength pigments, reduction in particle size should lead to a considerable increase in strength, particularly below 0.3  $\mu$ . It has been shown in practice that this does occur, but to different extents with different pigments<sup>3, 4</sup>.

Figure 1 shows the effect of increasing dispersion time related to colour strength and particle size with two pigments. A phthalocyanine blue shows a rapid increase in strength below an average particle size of 0.3  $\mu$  whilst on the other hand, a Pigment Green B shows a relatively small increase with the same particle size reduction.

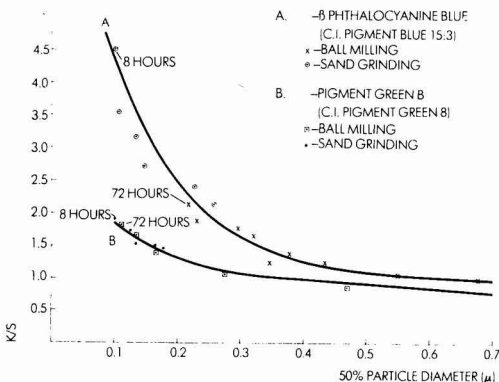


Figure 1. The dependence of colour strength on particle size.

Other conclusions can also be drawn from these curves.

- (1) Bead milling is more efficient than ball milling
- (2) The time of milling to achieve strength improvement may not be a commercially viable proposition.

In general, very appreciable strength increase is possible by reducing average particle size from approx. 0.5  $\mu$  to 0.2  $\mu$  (see Table 1), but having obtained a reduction in particle size, it is necessary to stabilise the dispersion so obtained. This is not always easy in practice, e.g. Arylide Yellow G/10G pigments do not produce fine dispersions easily, possibly due to flocculation, whilst phthalocyanine blue, particularly those of the alpha type, may show severe flocculation, depending upon the system and method of application.

Table 1  
Effect of particle size on colour strength

Pigment	Approximate increase in strength as size reduced from 0.5 $\mu$ to 0.2 $\mu$
Arylide Yellow 10G	135%
Arylide Yellow G	100%
o-Anisidine Yellow	275%
m-Xylylide Yellow	160%
Pigment Yellow 74	100%
Manganese 2B toner	150%
Calcium 4B toner	65%
Dioxazine violet	115%
$\beta$ -phthalocyanine blue	180%
Phthalocyanine green	85%
Pigment green B	50%

### Opacity

Opacity increases appreciably down to a particle size of about 0.2  $\mu$ , but then decreases rapidly. (See Fig. 2). With organic pigments, however, this is less than with inorganic types.

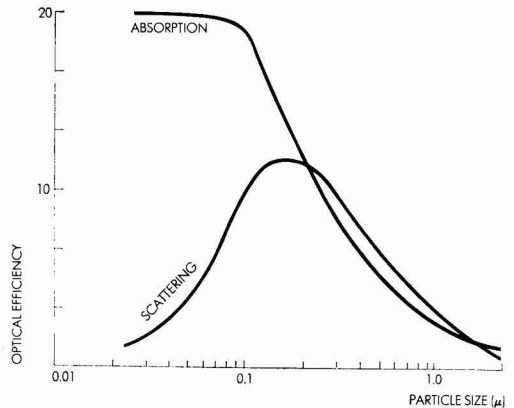


Figure 2. Effect of particle size on absorption and scatter of organic pigments.

### Flow

Flow is dependent upon pigment concentration and also on particle size. (See Fig. 3). It must be realised, however, that flow problems are more often affected by structure in the paint, due to instability of the dispersion. It is theoretically possible to reduce pigment concentration, increase dispersion and thereby produce increased colour strength at reduced viscosity.

### Gloss

Gloss has been shown to increase down to particle size levels of 0.3  $\mu$  but beyond this, further reduction in size has little effect.

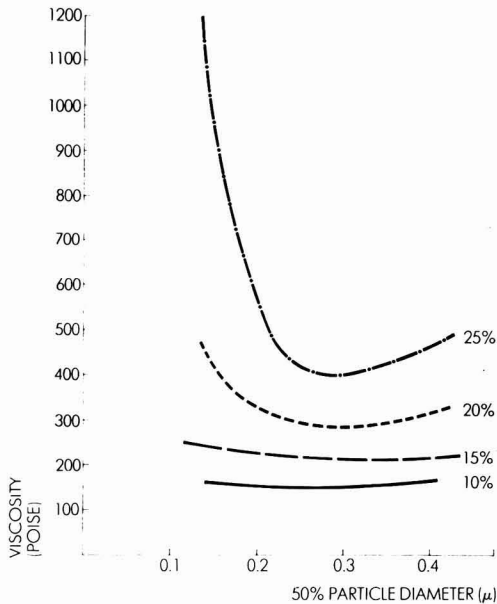


Figure 3. Effect of particle size on viscosity of different pigmentation levels.

To summarise, it can be stated that to give the most stable dispersions with the highest colour strength, the best gloss and adequate flow, the average particle size of organic pigments must be reduced to a level of 0.2 to 0.3  $\mu$ . It is, however, very time consuming and demanding on resources for any paint manufacturer to ensure that he has the optimum level of dispersion in all his systems, involving microscopic control as well as strength and gloss factors. Once an optimum performance has been achieved, batch testing can be controlled by simple comparisons of colour against the standard optimised result.

### Pigment manufacturers role

The optimum performance may be approaching the ultimate in terms of what is possible, but is it feasible and viable for the pigment user to do so? The situation can be considered

from the pigment manufacturer's point of view: He generally has the opportunity, by using surface treatment or modified isolation techniques, to reduce or even avoid the strong aggregation which often occurs when a pigment is isolated in a dry powdered state. This results in a more uniform, consistent product which provides the user with the capability of obtaining a more nearly optimised result. The pigment user may justifiably state that it is his job to disperse the pigment, but it must also be appreciated that it is the pigment manufacturer's role to provide the best possible product. The pigment manufacturer is often able to utilise different technologies in producing dispersed products and this can only result in benefits to the user.

There are various possibilities:

#### *Easily dispersible products*

These pigments are carefully controlled during manufacture. They usually contain small quantities of added resin or surfactant which enables the agglomerates to be broken down quickly and easily at the dispersion stage.

Various types are available commercially, and their advantages are easily apparent in terms of extra strength, extra gloss, and extra stability, as well as the lower energy input required to give a satisfactory dispersion. Unfortunately, not all pigments react to such treatment in the same way and it is not always possible to achieve the same degree of performance.

These pigments go part way towards producing the optimum properties, particularly in terms of getting improved results with less energy input. Cost of production is comparatively low and this is usually more than outweighed by the energy saving in use.

#### *Solid pre-dispersions*

These cover a wide range of products, in which the pigment is usually in a very fine state of subdivision in an appropriate carrier, which may be more than 50 per cent of the total composition.

There are many levels of quality, giving different degrees of performance, ranging from simple chip products and plastics master batches to the very high quality specialised materials put out by pigment manufacturers. The level of dispersion is much improved and in the best products available, is almost ideal. They have better gloss, better stability and above all,

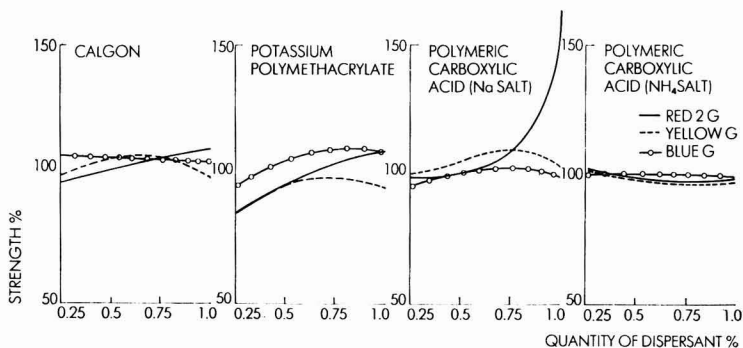


Figure 4. Effect of dispersant type and quantity on colour strength obtained.

better strength, usually combined with improved colour properties.

Whilst giving the colour user many of the desirable optimised properties, they are not necessarily the complete answer. The extra cost of these products can be justified only if their superior performance merits it.

#### Liquid preparations (aqueous)

Aqueous pre-dispersions have been available for many years and these are the nearest approach to a fully optimised dispersion. Pigments can be dispersed to a fine level and then well stabilised to give dispersions compatible with many aqueous systems and having good storage properties. However, it is not always appreciated that a dispersion, which in itself is stable, can be adversely affected by the system to which it is added. Dioxazine Violet is a typical example, and apparently stable dispersions can produce widely differing results, severe flocculation occurring with some commercially available emulsion paints, whilst being stable in others. To ensure

complete stability over the whole range of commercially used systems and considering the wide variety of white pigments, extenders, surfactants, colloids, coalescing agents etc. which may be present, is a daunting task. It can be shown that each component can have an appreciable effect. Fig. 4 shows the effect of various surfactants, Fig. 5 shows the effect of coalescing solvents, and Fig. 6 shows the effect on strength obtained with differing types of colloid.

#### Liquid preparations (multipurpose)

By relatively simple modification of aqueous dispersions, it is possible to make them compatible with both non-aqueous and aqueous air-drying systems. Such products are of considerable value in the DIY market, but it must be appreciated that to obtain this broader usage area involves a reduced overall stability. Unless the stainer is designed specifically for selected paint formulations, inferior performance in one or other system may occur, and such pastes are, therefore, often best produced by the paint maker to suit his own specific needs.

Multipurpose stainers have other problems which limit their overall applicability, and this will be discussed later.

#### Liquid preparations (non-aqueous)

Most pigment users make dispersions in non-aqueous media for their own use. In addition, several specialised dispersion manufacturers will provide a service in individual media, whilst certain pigment manufacturers will also supply pigments flushed in selected resin solutions. The first two use ordinary dry powders, but the flushed pigment processor does offer some positive improvements in terms of dispersion. It is still far from the optimum performance, however, and in addition such resin dispersions can have many inherent faults, such as low pigment content and, therefore, low strength, a tendency to dry out or skin (often wasteful unless used within a short time of manufacture), poor storage stability and a tendency to settle if they are too fluid or thicken up if too viscous, a tendency to give variable results depending on the consistency of the milling process and the quality of pigment used. They are usually produced in small batches only and are, therefore, expensive and they can show severe flocculation, thereby giving variable results depending on the resins used and the concentrations employed.

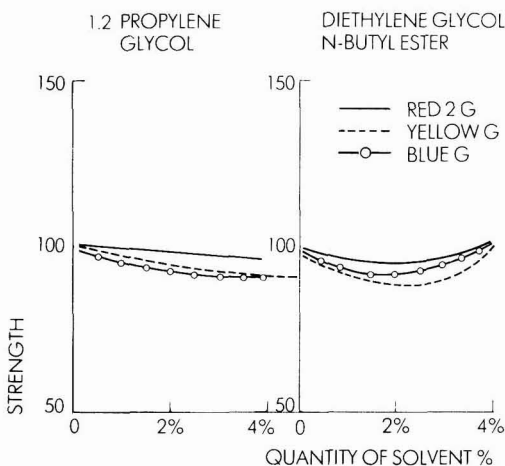


Figure 5. Effect of coalescing solvent on colour strength obtained.

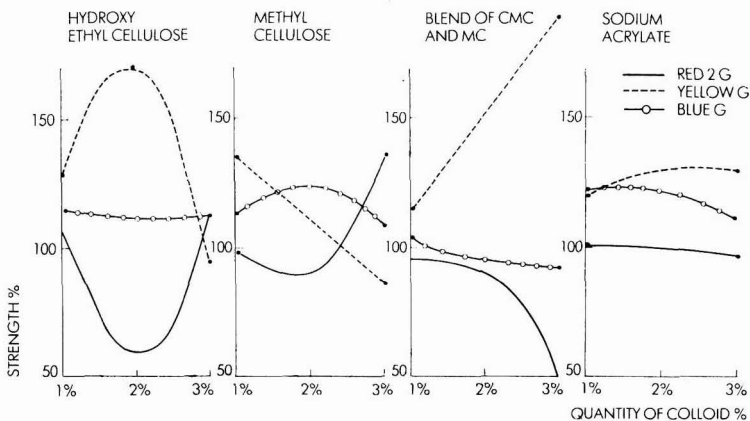


Figure 6. Effect of colloid type and quantity on colour strength attained.

The pigment manufacturer's technology and expertise has developed in this field and stainers are now available which overcome most of these faults. Although not yet being the ultimate in terms of dispersion and stability, these products are appreciably superior to those which have hitherto been available on the market.

### Concentrated solvent dispersions

*Refs. 5-9*

This range of dispersions can be described as high-strength, free-flowing, stabilised liquid dispersions for non-aqueous paints, particularly those decorative systems based on white spirit as solvent. They will be referred to as "Concentrated solvent dispersions". They are equivalent in alkyd-based finishes to the well established aqueous dispersions in decorative emulsion paints. They are solely for solvent-based paints and have been optimised and are standardised for white spirit based long-oil alkyds. In this respect, they differ from the multi-purpose stainers, of which there are already a number of proprietary brands available.

### Stabilisation

In the development of these products considerable emphasis has been placed on the stabilisation of the dispersion, as well as the optimisation of the dispersion process. With the majority of non-aqueous dispersions there is always a tendency for particle growth to occur during storage, either by flocculation, agglomeration or even crystal growth. Much depends upon the relative adsorption of the resin and solvent at the pigment particle surface<sup>5</sup>. If the resin is adsorbed and well bonded to the pigment surface, then good dispersion stability can usually be achieved, but if this adsorption is weak, the resin can be stripped from the surface and replaced by solvent, with consequent reduced stability and tendency towards flocculation. The problem is how best to achieve a resin layer at the pigment surface even in the presence of large quantities of solvent. The answer lies in the development of specific stabilisers giving multi-point attachment to the pigment surface. The basic "backbone" of the product is essentially insoluble in white spirit, but gives good adhesion to the pigment surface at several points. In addition, however, long chain attachments extend into the solvent giving a highly solvated unit of high stability (Fig. 7). In certain cases it is also found advantageous to include a further specific additive on the pigment surface which would improve the adhesion to the stabiliser nucleus. This results in the ability to produce highly stable dispersions containing the minimum of "additives" and a high white spirit content.

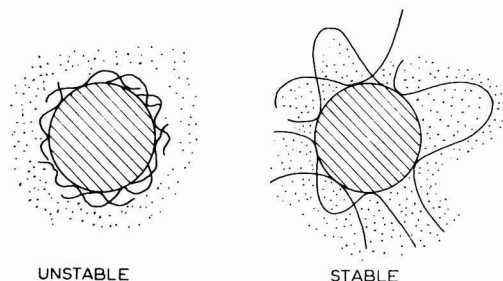


Figure 7. Stabilisation of dispersed pigment particles.

Such products overcome many of the problems which have been previously identified with conventional alkyd-based stainers. They are of low viscosity, having higher pigmentation and greater stainer strength. This in turn allows for the production of stronger coloured finished paints. They have no tendency to skin or gel, thereby giving less wastage, and they have excellent storage stability and show virtually no tendency to settle or to flocculate. They give a more consistent performance because the final dispersion is standardised by the pigment manufacturer. This facilitates their direct use in instrumental colour match prediction systems. There is no problem of batch size as the products can be provided as and when required in large or small quantities.

Optimising dispersion and stabilisation in this way provides many advantages over conventionally produced stainers. However, the future potential must be considered and also the implications with regard to conditions of work in the factory, less dust, less wastage and increased efficiency. There is potential for changes in factory layout and the flexibility of use allows the introduction of completely new procedures and working practices. The benefits to be gained can be illustrated by examining in more detail some of the technical properties of the Concentrated solvent dispersions.

### Pigmentation level

Table 2 compares the concentrated solvent dispersions with typical factory-produced stainers in terms of pigment content.

Obviously in this and in subsequent comments on factory produced stainers, it is difficult to generalise regarding what is normally obtained, but these figures are representative. In most cases, the Concentrated solvent dispersions have approximately twice the pigment content, yet they remain completely free flowing.

This high pigment content enables a higher ratio of coloured pigment to white pigment to be achieved without excessive dilution of the paint. It is quite feasible to produce the majority of the BS 4800 shades, including the strong shades by simple addition of these products to a white base.

### Ease of incorporation

Because of their low viscosity the Concentrated solvent dispersions can be incorporated very easily and simply into oil based decorative white bases or into clear lacquer by a low energy simple stirring process. In addition, the high stability prevents flocculation, giving uniform results irrespective of depth of shade. If a comparison is made at different shade depths in which the dispersions are added to a long-oil alkyd based white paint, using slow speed paddle stirring and high speed cavitation mixing, no difference is apparent in shade, strength or gloss, irrespective of the intensity of mixing or depth of shade involved. The Concentrated solvent dispersions are, therefore, highly robust to handle giving fully acceptable paints irrespective of the sophistication of the mixing equipment being used. It has been mentioned already that negligible flocculation occurs on addition of the stainers to a white base. Even the phthalocyanine blue stainer shows only slight flocculation, appreciably less than with a conventional stainer.

### Tinting strength

Table 3 indicates the comparative strength on the basis of equal pigment weight of the Concentrated solvent dispersions relative to laboratory stainers produced by conventional, but

Table 2  
Pigmentation levels of concentrated solvent dispersions compared with those of typical factory-produced alkyd stainers

Pigment	Pigment content of concentrated solvent dispersion Irgasperse S	Pigment content of alkyd stainer based on same pigment
Arylide yellow G C.I. Pigment Yellow 1	40-50%	15-20%
Arylide yellow 10G C.I. Pigment Yellow 3	40-50%	15-25%
Yellow oxide of iron C.I. Pigment Yellow 42	40-50%	20-30%
Red oxide of iron C.I. Pigment Red 101	40-50%	20-30%
Dinitraniline orange C.I. Pigment Orange 5	40-50%	15-25%
$\beta$ -phthalocyanine blue C.I. Pigment Blue 15:3	25-30%	5-15%
*Bon arylamide red C.I. Pigment Red 112	25-30%	10-15%
*Monoazo red C.I. Pigment Red 223	30-35%	15-20%
*Carbon black C.I. Pigment Black 6	25-30%	15-25%

\*Expected to be commercially available during the latter half of 1979.

Table 3  
Comparison of tinting strengths

Pigment type	Conc. Solv. Disp. (Irgasperse S) (1)	Laboratory stainer (2)	Factory stainer (3)	Multi-purpose stainer (4)
Arylamide yellow G Pigment Yellow 1	100 pts Control	125 pts Weaker	—	70 pts Stronger
Arylamide yellow 10G Pigment Yellow 3	100 pts Control	130 pts Weaker	—	—
Yellow iron oxide Pigment Yellow 42	100 pts Control	105 pts Weaker	115 pts Weaker	100 pts Similar
Red iron oxide Pigment Red 101	100 pts Control	105 pts Weaker	—	100 pts Similar
Dinitraniline orange Pigment Orange 5	100 pts Control	110 pts Weaker	—	—
$\beta$ -phthalocyanine blue Pigment Blue 15:3	100 pts Control	125 pts Weaker	130 pts Weaker	—
Bon arylamide red Pigment Red 112	100 pts Control	105 pts Weaker	135 pts Weaker	100 pts Similar
Carbon black Pigment Black 7	100 pts Control	105 pts Weaker	160 pts Weaker	—
Monoazo red Pigment Red 223	100 pts Control	115 pts Weaker	—	—

optimised, ball milling of the base pigments, factory produced stainers randomly obtained from paint manufacturers in the UK, and multi-purpose stainers commercially available.

It will be seen from columns (1) and (2) of Table 3 that in every instance the Concentrated solvent dispersion is stronger than a conventionally produced, but optimised laboratory

ball milling of the same base pigment. It is generally to be expected that laboratory millings give better dispersion and, therefore, higher strength than factory-produced stainers, and this too is confirmed by comparison of columns (2) and (3). In practical use the specialised dispersions, therefore, offer even greater advantages than in the laboratory. Finally, the strengths of certain multi-purpose stainers show them to

be similar to the new solvent based products. This is to be expected as they, too, are optimised in preparation but as stated earlier, they do have certain faults with regard to their use in alkyd-based systems.

In the case of the Arylide Yellow 10G, it has also been possible to consider the consistency of strength development more fully (Table 4). Use of the Arylide Yellow 10G dispersion tinted by three different paint manufacturers has shown that in every case an equal strength result is obtained, which is also equal to that obtained in the laboratory. If, however, dry pigment is purchased and converted to a tinter, widely differing results are produced depending on the quality of dispersion and in every instance the factory result is weaker than the laboratory result.

**Table 4**  
Factory trials on Arylide yellow 10G  
Concentrated solvent dispersion

	Arylide yellow 10G Dry powder	Conc. solvent dispersion (Irgasperse yellow 10G-S)
Laboratory result	Stronger 70:100	100 Control
Factory result 1	Stronger 90:100	Equal 100:100
Factory result 2	Equal 100:100	Equal 100:100
Factory result 3	Weaker 120:100	Equal 100:100

Table 4 also indicates an additional point. The 10G pigment used in all the factory stainers was the easy dispersible quality mentioned earlier, which would be expected to give appreciably stronger results than the normal quality used in the solvent dispersion. As recorded in Table 3, the laboratory produced stainer of the same pigment grade as that used in the dispersion is weaker (130:100) than the concentrated solvent dispersion. Despite the easier processing of the yellow used in the factory stainers, a stronger result is not always obtained.

The higher strength obtainable per unit dry weight of the pigment in the Concentrated solvent dispersions, allied to the higher pigment content compared with alkyd stainers, emphasises the advantage which can be obtained by using the new dispersions in strong shades without excessive dilution of the finished paint.

**Particle size distribution**

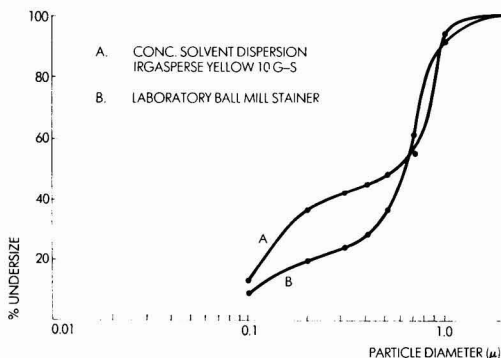
To demonstrate further the advantages in particle size reduction obtained in these solvent dispersions, particle size distribution measurements have been made using the Joyce-Loebl Disc Centrifuge. This uses a centrifugal sedimentation technique which has been described by various workers<sup>6-9</sup>.

Three product groups have been examined:

Fig. 8 illustrates the Arylide Yellow 10G pigment. Clearly the Concentrated solvent dispersion has a finer particle size distribution than the laboratory produced stainer. The mean particle size is often expressed as the 50 per cent diameter, i.e. the diameter above and below which there is 50 per cent of the pigment by weight. In this instance, the figures are:

- Laboratory ball milled stainers — 0.61  $\mu$
- Concentrated solvent dispersion — 0.54  $\mu$

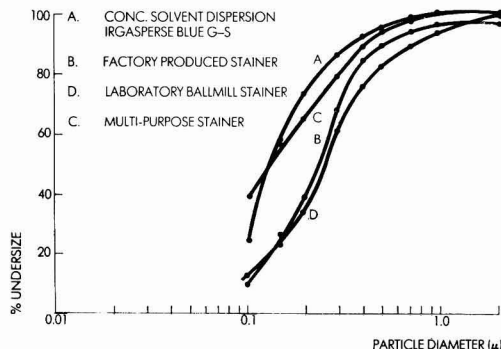
It will be observed that the ideal level of 0.3  $\mu$  is not achieved here, but this is a balance between dispersion and weatherability.



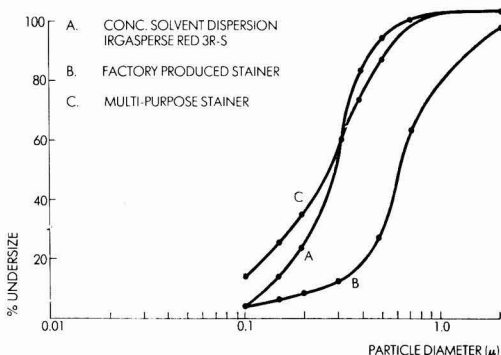
**Figure 8. Particle size distribution curve. Arylide yellow 10G. C.I. pigment yellow 3.**

Figure 9 shows the situation for  $\beta$ -phthalocyanine blue. The Concentrated solvent dispersion is similar to the Multipurpose stainer as would be expected, whilst both are appreciably superior to conventional ball millings.

- The 50 per cent diameters were as follows:
- Laboratory ball milled stainer — 0.26  $\mu$
  - Factory produced stainer — 0.24  $\mu$
  - Multipurpose stainer — 0.13  $\mu$
  - Concentrated solvent dispersion — 0.13  $\mu$



**Figure 9.  $\beta$ -phthalocyanine blue C.I. pigment blue 15:3**



**Figure 10. Bon Arylide reds C.I. pigment red 112**



Figure 10 illustrates the distribution curve for stainers based on a Bon Arylamide Red. Again the specially developed products are both appreciably superior to a factory produced stainer. The 50 per cent diameters were as follows:

Factory produced stainer	—	0.60 $\mu$
Multipurpose stainer	—	0.27 $\mu$
Concentrated solvent dispersion	---	0.28 $\mu$

It must be emphasised once more that the figures quoted for factory stainers are included only to give a trend indication. Individual stainers will obviously vary and some products may approximate more closely to the specialised ranges in terms of dispersion.

#### Gloss and gloss retention

Stabilisation has been stressed in these Concentrated solvent dispersions as being an indication of good wetting by the resin system. A further indication of this is provided by the good gloss and gloss retention of paint panels produced from strong shade paints. Arylide Yellow G pigments are well known to be liable to give poor gloss retention, and the solvent dispersion of the same pigment gives a much improved result (Table 5).

Table 5  
Gloss and gloss retention of strong shade paints  
based on Arylide yellow G

Storage period (23°C at 45% R.H.)	Conventional laboratory Ball milling	Conc. solvent dispersion Irgasperse yellow G-S
Initial	80%	85%
1 week	65%	84%
2 weeks	55%	80%
4 weeks	50%	75%

#### Storage stability

All the Concentrated solvent dispersions have been stored

(a) At room temperature for 12 months

(b) At 40°C for 3 months

They have all been found stable, showing no colour drift or strength variation, and to be essentially free from sedimentation or separation with no tendency to flocculation.

#### Compatibility with other systems

These pigment dispersions are based on white spirit and are directed primarily towards the decorative alkyd based paint

market. However, they obviously will be compatible with several other paint systems.

Several possibilities have been investigated briefly and the indications are that in many instances success is possible. It will be necessary to check individual systems, but the following brief comments can be made:

- (1) Urethane alkyd—no problems experienced with a urethane oil modified linseed alkyd based on white spirit.
- (2) Vinyl toluene alkyd—better gloss and gloss retention obtained, but care may be necessary if aromatic solvents are used.
- (3) Gel alkyd—no adverse effects observed on the gel structure. This is a further positive advantage over the multi-purpose type of product.
- (4) Styrenated alkyd/alkyd-melamine—show adequate compatibility, but the choice of pigment is critical and the strong solvents reduce some of the advantages shown in white spirit based systems.

#### Conclusions

It is the intention in this paper to indicate that appreciable improvements in technical properties can be obtained if pigments are correctly dispersed and stabilised. Although it is desirable to have products with a wide range of application in widely differing systems, this does not necessarily give the best effect. The Concentrated solvent dispersions represent a more ideal stainer type product which has been developed specifically for alkyd based paints and in this particular outlet superior performance results.

It is probable that the ultimate has not yet been reached. The ideal is always better than that which is currently available, but the pigment manufacturer has probably the greatest chance of approaching this ideal by development of specialised dispersions.

[Received 12 March 1979]

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#### Discussion at Stratford Conference

DR G. D. PARFITT commented on the suggestion that the particle size required to give optimum performance of dispersed organic pigments was about 0.2 micron. He was interested to note that this is the same size as required for TiO<sub>2</sub> pigments, as predicted by light scattering theory. However, for TiO<sub>2</sub> the basic crystal size as manufactured is 0.2 micron and in the dispersed state only a fraction of the pigment is normally present as single crystals, the main part being aggregates of larger size. For an organic pigment, however, the basic crystal size is usually much less, and so for the optimum size of 0.2 micron the pigment must be present as aggregates.

He asked if there was any information available on the thickness of the stabilising layer of polymer on the pigment surface, and if the polymer had been designed in terms of chemistry and size to give the optimum thickness and ultimate steric hindrance effect.

MR VARLEY stated that the particle size figures quoted were related to the average particle size, primarily obtained by centrifugal methods. They are not the crystal sizes, but the sizes of the agglomerates within the dispersion. He said that there were benefits to be obtained by going to smaller particle sizes, but there were also problems, such as with

flow and transparency, and the figure given was a compromise to achieve the best overall performance, applicational performance and usage performance in terms of opacity, hiding power etc. 0.2 microns appeared to be the size to which the wavelength of light began to have an effect, so that smaller sized pigments would produce transparent films.

Referring to the thickness of the absorbed layer on the pigment surface, Mr Varley stated that the choice of additives was limited, but an empirical approach had been taken to determine what would give the optimum performance in the dispersion, i.e. with good stability, and good strength from a reasonable grinding period, etc. The actual thickness of the absorbed layer, whether di-molecular, tri-molecular etc., had not been measured.

MR A. SAARNAK asked if the stabilising polymer layer was anchored well enough to the pigment surface to withstand more polar solvents than the white spirit, or if it would be dissolved away by stronger solvents.

MR BOWER answered that it could be used with other systems, but it had not been designed for the more polar solvents, and so they would probably not be optimised for such systems.

MR VARLEY added that they had tested the dispersions in a variety of different systems, including styrenated alkyds, vinyl toluene alkyds and alkyde melamine systems, and although they had not been designed for such types, very acceptable performance had been obtained with phthalocyanine blue and the other pigments which are suitable for use in the presence of strong solvents.

MR D. A. KALWIG asked if, in the future, tinting systems for industrial coatings would be available, such as had been available for the general decorative market. Specifically, economical pigment dispersions to be used to make up a variety of industrial small orders, for use in a wide variety of systems. He also asked if pre-dispersed pigments would be available for use in total pigmentation as well as for tinting purposes.

MR VARLEY stated that dispersions had been available for a number of years from various manufacturers which could be used as tinters, or even dry tinters, but often these products are not economically viable. At present, he was unable to say that this system would definitely be available for this purpose, but there seemed to be no reason why the approach used for air drying decorative paints could not be applied equally well to this industrial application.

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## Next month's issue

The Honorary Editor has accepted the following papers for publication, and they are expected to appear in the November issue of the *Journal*:

**Aluminium compounds as major components of surface coatings** by *J. H. W. Turner and W. K. H. Lakin*

**Dry-on-wet—A new concept in low pollution coatings utilising cellulose acetate butyrate** by *B. P. Windibank and R. W. Mahar*

**The changing role of polymer chemistry in organic coatings technology** by *M. F. Kooistra*

**Scanning electron microscope study of a coating component deposited from solution into wood** by *M. H. Schneider*

### Count their legs and divide by four

Sir—"The Exhibition was attended by 8 000 000 millipersons. It was open for 0.011 year. There were 7500 centistands which were manned on most days for 28 800 seconds. The entrance fee was 400.00 halfpence for non-members, which entitled them to a catalogue weighing 153 200 mg."

Is this statement any more ridiculous than is the habit of quoting large linear measurements in millimetres, or viscosities in centipoise? How many people can distinguish between one and fifty cP., let alone any less significant increment?

Those of us who were brought up with the CGS system realise how impractical are the present "fashionable" terms. The CGS method allowed for the use of multiple and fractional units where applicable. A centimetre is something that the ordinary person can visualise. Longer lengths should be expressed in metres or multiples thereof. (Another irritating custom is that of putting the accent on the second syllable of the compound word "kilo-metre".)

Grams and kilos are practical terms and so are poises. But stick an impressive row of noughts on the end and the whole expression becomes meaningless until one has

mentally converted the figure back to a more sensible one. It is bad enough having poises, stokes and pascals quoted in the literature (not to mention all the other units of viscosity dearly beloved by the petroleum and other industries). But the *unnecessary* introduction of tiny subdivisions merely adds to the confusion. Is 2000 milliamps any better than 2 amps?

Can't we keep the centipoise for viscosities of less than a poise, and the millimetre for small lengths under a centimetre? Is not 43 cm a much more "meaningful" figure than 430 mm? Doesn't 500 poise mean more to the varnish chemist than 50 000 cP? Why can't we maintain the old practice of using a term which is of the same order of magnitude as the quantity being measured, so that the minimum number of integers is required?

Who ever gave the area of a field in square feet or the span of a lifetime in minutes? We have an adequate supply of practical-sized terms. Let us use them.

Yours faithfully,  
W. F. DAGGETT

3 Barn Close,  
Littlehampton,  
West Sussex

8 August 1979

## Reviews

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### Law of industrial pollution control

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A. Walker

George Godwin Ltd, London 1979

Pp xx + 194 Price: £10.00

Should a law textbook be interesting? That it can be is undoubted; we need not go beyond anything written or edited by Winfield or Cheshire. Whether it should be or not may depend upon its object: the requirements of a practitioner's working handbook and of a student's text are inevitably different. The present book claims to be written as a handbook for the "plant manager" (presumably the author means "works manager") and the bureaucrat.

And, of course, it is much easier to make Common Law interesting than statutory law—especially when the Statutes are recent and have gathered no case law around them. So the present author is faced with a fairly arid area; the important Acts are no earlier than 1974, and for various reasons have not attracted much case law of value. He thus must set doggedly about summarisation of the relevant Acts—which he does adequately, solidly and quite uninspiredly, with a somewhat boring habit of spelling out the penalties quantitatively in every case. For the manager or Managing Director who wants no more than to read of his obligations and liabilities in epitome this is an excellent book.

The author devotes one chapter to Common Law, which still governs private rights in matters of pollution—and which was controlling under the heads of Nuisance and Negligence long before any statutory control existed. It is not clear why he is so dismissive about its value today; your reviewer would have thought that the threat of civil

damages (which are unlimited in amount) could be much more potent than the liability to a fixed criminal penalty. Another rather strange thing is that the author never criticises or comments on any of the legislation; it is, after all, not perfect, and some indication of ambiguities, anomalies and loopholes would surely be of value.

M. H. M. ARNOLD

### Hess's paint film defects. Third edition.

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Edited and revised by H. R. Hamburg and W. M. Morgans

Chapman & Hall, London 1979

Pp xiv + 504 Price: £25.00

For the past 30 years, paint technologists encountering an inexplicable paint defect for the first time have been turning to Hess's Paint Film Defects.

As new types of paints are developed they bring new defects, so the work needs occasional revision to keep pace with advancing technology. This is the reason for this third revised edition which now covers subjects such as powder coatings, high-build coatings and radiation curing. The revision is substantial and has been carried out by Dr Hamburg and Dr Morgans, assisted by others.

The size and form of this edition is similar to the previous one, proceeding from faults which develop during storage of the paint to faults arising during application and faults developing on the coating in service. In this connection it might be considered that the title of the book does not fully cover its scope as part of the work is concerned with defects of the liquid paint (before any film is formed). The full

subject index is invaluable and the references have been well up-dated.

The book is invaluable for diagnosing paint faults, but it cannot, of course, always provide the remedy, as this may not be known within the present state of the art. It is an essential buy for any paint laboratory and the previous edition could well be passed on to someone who could still make good use of it.

L. A. O'NEILL

### **Handbook of electropainting technology**

**W. Machu**

**Translated from German by P. Neufeld**

**Electrochemical Publications Ltd, 1978**  
**Pp xi + 307**

This standard book of reference was first published in Germany five years ago. The English edition has now been carefully and competently translated by Dr Neufeld and the result is an excellent and authoritative account of electropainting technology which will be of value to most industrial paint chemists. Close checking for typographical and grammatical errors in the main text has eliminated the common faults of direct translation; the English style and presentation is first class. The table of contents is the only section where mistakes have not been corrected, but this is a minor criticism which does not detract from the generally

favourable impression.

A brief historical account of electropainting is followed by five chapters describing colloid electrochemistry, deposition processes, voltage and current relationships, throwing power and bath control parameters. Pretreatment is very well covered and this reflects the prime interests of the author.

Cathodic deposition of paint is described, but this section is unfortunately out of date due to the significant technical advances which have occurred in the last three years. Short chapters are devoted to one coat and two coat application followed by a section describing the problems of resin binder selection in paint formulation. Plant installations, mainly in Continental Europe, are illustrated with a number of well-known examples and the following chapters fully describe the processing techniques. Effluent treatment is discussed with the emphasis on ultra-filtration methods.

Drying ovens and voltage control are adequately covered and the book concludes with a review of economic considerations and patent references for process, plant and paint compositions.

Safety is a notable omission which should be included in the almost inevitable second edition.

The volume is well designed with good printing and binding.

S. T. HARRIS

## **Section Proceedings**

### **Manchester**

#### **Carlton open day**

The invitation from BTP Tioxide Ltd for Manchester Section members and their guests to visit their Carlton Weathering Station, Teesside, on 6 June 1979 was accepted by approximately 30 members. The warm friendly reception by Harry Fuller, who is in charge at Carlton, and his colleagues contrasted sharply with the cold North East weather conditions on the site.

A report of the work being undertaken at the Weathering Station appeared on page 324 of the August issue of *JOCCA*. Appreciation of these facilities were gratefully acknowledged by those members and guests who visited Carlton.

#### **Student visit to Synthetic Resins Ltd**

The laboratories and production facilities of Synthetic Resins Ltd, situated at Speke, Liverpool, were visited by 19 members, some from bygone student times, on 14 June 1979.

Welcomed initially by Tony Jolly, the Section Chairman who is also Technical Sales Manager, Surface Coatings Division at SRL, the visit continued with an historical introduction to the company by Mr W. Flamson. He

described how David Koller joined Emil and Rudolf Beck to form Beck Koller in 1868, followed by an association with Karl Reichold in 1872 to found Reichold Chemicals. Initial production in the USA, including supplies to Fords, was followed by production facilities in Liverpool during the 1930's. The present role of the company as a subsidiary of Unilever was preceded by the amalgamation of Beck Koller Ltd with Chas Lowe and Styrene Co-polymers Ltd in 1969.

The product range exceeds 300 resins ranging from alkyds to zinc rosins via polyesters, epoxides, urethanes, elastomers, phenolics etc.

During the conducted tour of the factory, which is based on a gravitational flow system, the two most impressive features were quality control and safety precautions. The former is achieved by plant control, a QC laboratory, R & D laboratories and pilot plants. The latter was very evident from the mandatory use of protective clothing, mini-fire stations, storage areas isolated during tanker deliveries together with the usual surrender of matches/lighters before entering the plant.

This visit was concluded by excellent refreshments in the Conference Room. Incidentally, the comprehensive nature of this visit obliged SRL reluctantly to decline two applications from employees of competitive companies. The Manchester Section is indebted to the Directors and Staff of SRL for permission to visit their factory.

F.B.W.

# Information Received

## New polymerisation plant

Witco Chemical Ltd has announced the completion of a new solution polymerisation plant for the production of urethane coatings and adhesives at their Droitwich site.

The plant uses technology and design data developed by ICI and licensed from ICI to give close control of viscosity and other properties required to make products of a consistently high quality.

## Agents appointed

Conoco Chemicals Europe SA have appointed Alfa Chemicals Ltd exclusive UK distributor for their range of drum quantities of o-cresol, cresylic acid and blends and their phenol based anti-oxidants.

## Bee Chemical expansion

The Bee Chemical Company has announced a \$1 million plant expansion programme at the headquarters location in Lansing, Illinois. Bee is a leading manufacturer of industrial coatings for plastics and metals, and the Injecta Color System which includes liquid colourants for plastics and precision metering pumps.

The expansion will triple the size of resin and dispersion capacity to meet increased demands from the industry.

## Molteni and Ge-Halin

D.H.Industries Ltd, part of the Steeltley group, are taking over the UK distributorship for the ranges of plant produced by Molteni and Ge-Halin. D.H.Industries will be able to provide demonstration, technical back-up, spare parts and service engineering for the machines and will be retaining Mr. G. J. Erlich, formerly the UK agent for the ranges, in a consultative capacity.

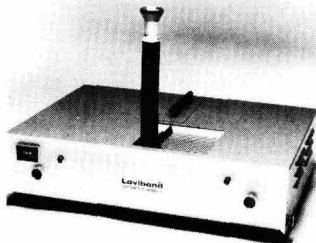
## Plant expansions

Two new plant expansions, costing over £1 million, are due to come onstream at the Oldbury site of Albright & Wilson Ltd. The production capacity of the disodium pyrophosphate plant has been increased by over 25 per cent and a new type of unit has been installed to make the product from monosodium phosphate by heat conversion. The second plant to be expanded is that producing phosphorous pentasulphide, which is used in the manufacture of oil additives and ore-floatation agents.

## New products

### New visual colorimeter

A new Tintometer designed to provide easier and more efficient colour measurements of liquid and solid samples has been announced by Tintometer Ltd. Tintometer Model E AF 900 includes a number of new features, such as the incorporation of



**The Tintometer Model E visual colorimeter from Tintometer Ltd.**

Lovibond red, yellow, blue and neutral tint glass filters into the filter racks, which are claimed to enhance its reliability and improve its operating facilities.

The liquid sampling handling facilities have been improved with the provision of a detachable cell holder with a built-in cell retainer which reduces the risk of liquid spillage within the instrument.

### Solid state flow alarm

Litre Meter has available a new flow alarm, the Litre Alarm, which is an entirely solid state device for use wherever any equipment requires a continuous flow of fluid, and is activated when the flow rate drops below an adjustable safe level.

The alarm has a probe with a shielded thermistor in the end, which is inserted into the fluid. The flow passing this sensor tip, which is heated by a small current, causes a reduction in its temperature proportional to the rate of flow. If the flow rate falls, the rising temperature operates a solid state switch which operates the alarm system.



**The new all solid state flow alarm introduced by Litre Meter**

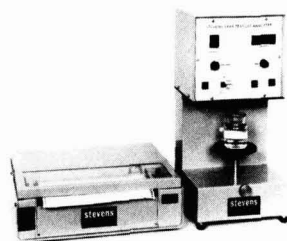
### Safer solvents

Hopkin and Williams have announced that they are now able to supply both "Inhibisol" and "CNP30" safety solvents,

which are recommended by Maxwell as safer substitutes for xylene, chloroform, propylene, etc and for clearing agents in optical and electron microscopy.

## New texture analyser

A new analyser made by Stevens Weighing Machines Ltd, originally designed for measuring the texture of foods, has been found to have a wide range of applications in industry.



**The Stevens Weighing Machines texture analyser with chart recorder**

Called the Stevens LFRA Texture Analyser, the new instrument has been developed in conjunction with the Leatherhead Food Research Association and is designed to perform a variety of tests where probes of various sizes are pressed into or on to products to determine factors such as gel strength, breaking point, hardness and consistency.

The range of probes which can be fitted to the instrument and the adjustable probe speed and sample penetration distance, give a high degree of versatility and the machine has been used with thixotropic paints, printing inks etc.

The instrument has a digital readout, can power a chart recorder and is claimed to give high accuracy and reproducibility.

## New gonioreflectometer

Anton Paar KG has available the new Gonioreflektometer GR-COMP, which is a new microprocessor controlled measuring device for the optical properties of glossy paint surfaces. The patented gonio-photometric method of operation, combining the ease of handling offered by a reflectometer with the powerful capabilities of a goniophotometer, offers for the first time separate and quantitative readings for specular reflectance, levelling and haze.

The built-in printer delivers error messages and operating instructions, thus allowing the instrument to be used by unskilled operators, and the results recorded include both the arithmetical mean and the standard deviation.

The instrument is capable of giving reflectometer values to DIN 67530, ASDN D 523/67 and ISO 2813 standards

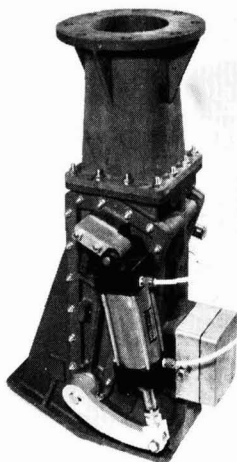


**The microprocessor controlled Gonioreflektometer GR-COMP for measuring the optical properties of glossy paint surfaces.**

for both 20 and 60° measuring angles. The machine also has several options available for special surfaces, such as for the measurement of "metallic effect".

#### **Powder diverter valves**

A new design of flap diverter valve for bulk handling systems, which has the sealing qualities of a plug valve yet is equally suitable for use with powders or granules has been introduced by Bush & Wilton Valves Ltd.



**The new design flap diverter valve from Bush & Wilton Valves Ltd.**

The new type DC valve is available in materials such as iron, stainless steel, bronze and aluminium in sizes from 100 to 300 mm, and contains several design features, thought to be unique in this type of valve. These features enable it to function as a reversible sealed unit, under pressure or vacuum, but without the problem

of clogging, which makes plug diverters unsuitable for powders, or of rapid seal wear, which is a characteristic of conventional flap diverters.

#### **Conferences, courses etc.**

##### **Radio frequency drying**

PIRA, the research association for the paper and board, printing and packaging industries, has recently issued a report on an investigation into the applicability and economics of water-based adhesives used on existing laminating machines modified for radio frequency drying.

The experimental work demonstrated that it is practical to use rf radiation to dry water-based adhesives, and that a saving in space may be made over conventional machines which use hot air to dry solvent adhesives.

##### **Thermal analysis studies**

Perkin-Elmer has available Thermal Analysis Application Study 28 which describes the ASTM method for screening of potentially hazardous materials. The report details the methods and test instrumentation required to determine the kinetic constants which characterise the decomposition reaction and shows that differential scanning calorimetry is particularly well adapted to screening materials for possible explosive hazard.

Another application study, number 27 entitled "Use of the system 4 microprocessor controller in the thermogravimetric analysis of plastics, additives and fillers", is also available, and outlines the applications of TGA for the analysis of plastic and rubber fillers, additives and reinforcing agents.

##### **TTB Annual Lecture**

The Annual Lecture of the Technical Training Board of the Society of British Printing Ink Manufacturers will be held

this year on Monday 5 November at the Royal Society of Arts. The speaker will be Mr Colin Bloy of Johnson & Bloy Holdings Ltd and the subject will be "Printing inks—A history".

#### **Magnetic stirrers**

ChemLab Instruments Ltd have published a new leaflet describing their range of magnetic stirrers, including the Model SS3HT hotplate magnetic stirrer which is fitted with a temperature sensing probe.

#### **Twin screw extruders**

Baker Perkins Inc., of Michigan, USA, has available copies of a paper entitled "Energy control in twin screw extruders" by D. B. Todd, which describes work undertaken to develop an additional and improved mode of control for twin-screw compounding equipment to allow "fine tuning" of the equipment to accommodate changes in feed rate and feed properties without having to alter screw configuration.

#### **Corporate booklet**

Vinyl Products Ltd has recently published a corporate booklet featuring their production and laboratory facilities at Carshalton and Warrington. The booklet also illustrates some of the many end-uses for their range of Vinamul and Vinacryl synthetic resin emulsions.

#### **Appointments**

Mr John Hogg has been appointed General Manager of Albright & Wilson Intertrade Ltd, which was set up in January to facilitate Albright & Wilson's growing business with the Eastern European Socialist Republics.

Mr Hogg has worked with Albright & Wilson for ten years, and was previously the first Manager of Albright & Wilson GmbH in Frankfurt.

Mr F. G. Pickering, formerly with ECC's Research and Development Department in the PRP Technical Service Section, has been appointed as ECC International's Marketing Manager for the Paints and Polymer Section.

Dr Keith W. Humphreys has been appointed as Corporate Managing Director of Ciba-Geigy Plastics and Additives Company, and becomes a member of the Board of Ciba-Geigy (UK) Limited.

Dr Humphreys joined the company in 1959 as a research and development chemist working on synthetic resins. He later transferred to sales and, after a period as General Sales Manager, was appointed Deputy Managing Director of Ciba-Geigy's UK Plastics Division in 1971. He was later appointed Managing Director of the Division, and has spent the last year on assignments with Ciba-Geigy operations in the USA and Switzerland.





# OCCA-32 Exhibition

13-15 May 1980 Cunard International Hotel  
Hammersmith, London W6

*Many applications received from UK and overseas in enthusiastic response to new arrangements*

## Closing date for applications 30 November 1979

Within the first week of the Invitation to Exhibit at the OCCA-32 Exhibition being despatched, applications to take space had been received from many companies for each of the various types of facilities available, in the most enthusiastic response to the Exhibition yet experienced.

Amongst these companies, including multi-national organisations, from which applications for space have been received, are a number that have not shown at an OCCA Exhibition for several years, as well as more regular participants.

The new venue for the 1980 Exhibition will be the Cunard International Hotel, Hammersmith, London W6, and the main part of the Exhibition will be in two sections: on the ground floor, forming the entrance to the Exhibition, traditional style stands will be accommodated in the New Exhibition Hall where exhibitors of heavy machinery, plant and equipment will be located; on the first floor of the hotel, in the Queen Mary Suite, the stands will be of a simplified nature with the objective of allowing exhibitors to use modular display systems. These stands will have no platform, being erected directly on to the carpeted Suite floor, and so it will not be possible for heavy equipment to be displayed in this section.

Access between these two areas will be through the intermediate Mezzanine floor, where there are a number of rooms for companies to display free standing exhibits. These rooms were amongst the first to be requested, and have been

allocated to companies, the deposits already having been received.

In addition, there will be several suites and syndicate rooms on the third floor of the hotel, either for companies who wish to use this type of facility to exhibit, or for those who wish to have somewhere convenient to entertain their visitors in addition to their main stands elsewhere in the Exhibition. Already, several organisations have taken advantage of this opportunity to have a main stand for general enquiries, and the more private room for detailed discussions.



### Dates and times

The thirty-second annual OCCA Exhibition, a three day event, will be open as follows:

Tuesday 13 May 1980 ..... 09.30 to 17.30  
Wednesday 14 May 1980 .09.30 to 17.30  
Thursday 15 May 1980..... 09.30 to 17.30

### Theme for the Exhibition

*Motif:* The motif, designed by Robert Hamblin, uses the compass to symbolize the unique attraction of the OCCA exhibitions which annually draw exhibitors and visitors from numerous countries.

The aim of the Exhibition is the presentation of technical and commercial information relating to raw materials, plant and equipment used in the paint,

polymer, printing ink, colour, adhesive and allied industries, both in manufacture, processing and application.

The Exhibition Committee will be particularly pleased to welcome exhibits relating to the new energy efficient, low polluting technologies, including powder coatings, high solids coatings, radiation curing, water-based coatings and other developments.

### Applications Received

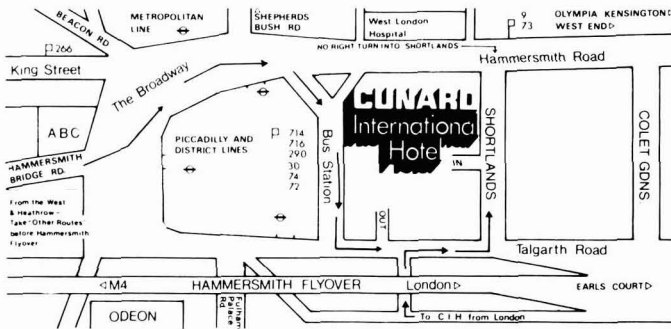
The response to the Invitation to Exhibit has already been very favourable and applications for space to be allocated in all sections of the Exhibition have been received from many companies within the first few weeks. Amongst those applications which have already been registered are:

- Baird & Tatlock (London) Ltd
- British Industrial Plastics Ltd
- Coulter Electronics Ltd
- Cray Valley Products Ltd
- Foscolor Ltd
- John Godrich
- H. Haeflner & Co. Ltd/Swada (London) Ltd
- Harlow Chemical Co. Ltd/Resinous Chemicals Ltd
- Hercules Powder Co. Ltd
- Industrial Dispersions Ltd
- K & K Greeff Industrial Chemicals Ltd
- Kronos-Titan GmbH
- Paint Research Association
- Paintmakers Association of Great Britain Ltd
- Q-Panel Co.
- Shell Chemicals Ltd
- Silberline Ltd
- Society of Dyers & Colourists
- Synthetic Resins Ltd
- Toxide International Ltd
- Victor Wolf Ltd
- Vinyl Products Ltd
- Werner & Pfleiderer (UK) Ltd

In addition, many other companies have indicated their intentions to participate, and many are having their applications processed. These applications are to show products as varied as resins, pigments, equipment, solvents and additives, and have come from some companies returning to the Exhibition after an absence of several years, as well as from more regular exhibitors.







Companies intending to apply for exhibition space are reminded that the closing date for applications is 30 November 1979, and shortly after this date the Committee will meet to make the first allocation. Preference for stand shapes, etc. will naturally be given to early applicants.

### The Cunard International Hotel

The Exhibition Committee has decided to move the venue of the 1980 Exhibition to the Cunard International Hotel, as it is felt that the more central site and greater range of types of exhibiting facilities it offers will be welcomed both by exhibitors and visitors to the Exhibition.

The Hotel has a selection of restaurants, shopping facilities and bars. There is a coffee shop immediately adjacent to the Queen Mary Suite (which itself contains a bar), an Exhibitors' Lounge on the Mezzanine floor, and there are plans for a coffee bar to be erected in the New Exhibition Hall for the Exhibition.

The Hotel is situated near Hammersmith Station on the Piccadilly Underground Line between Heathrow Airport and the centre of London. Visitors from overseas may board the Piccadilly Line in the Airport complex, which will take them direct to Hammersmith Station or to central London where they may be staying. Hammersmith Station is also served by the Metropolitan and District Underground Lines (the latter of which connects to Victoria Station for those arriving at Gatwick Airport). The Hotel is adjacent to the Hammersmith flyover on the M4 Motorway which links Heathrow Airport by road. Car parking at the Hotel is limited, but there is a large NCP car park close by in King's Mall off King Street.

Admission to the Exhibition will be free, and visitors will be asked to complete registration cards which will be available from the Association with copies of the *Official Guide* in advance. Copies of the *Official Guide* will be charged at £1.50 each, and both registration cards and copies of the *Official Guide* will also be available at the entrance to the Exhibition.

### The Annual Exhibition

The OCCA Exhibition is recognised as the world's most important international exhibition for the surface coatings and related industries, and annually provides companies with the opportunity to display their products and services and discuss them with visitors from many parts of the world.

*"... we obtained countless inquiries from representatives from nearly 30 different countries"*

In recent years, the Exhibition has regularly attracted visitors from over 50 countries, with a remarkably high proportion of top personnel from both the UK and overseas attending. The value of exhibiting need hardly be stressed when it is considered that it is possible, at this one annual event, to contact and maintain contacts with companies involved in the surface coatings industries from all over the world.

*"... the accomplishments of the first day alone were enough to justify our participation in the Exhibit, and I should also point out that the subsequent days were even better ..."*

"Anyone visiting this exhibition (OCCA-31) could not have failed to be impressed by the spacious and comfortable layout and the ease with which one could identify individual stands. For those whose range of interests includes all of the varied displays, to be able to see at a glance individual stands and the personnel available for discussion and yet at the same time, while promenading, enjoy the many re-unions is recognised as another of the unique characteristics of this annual event. The atmosphere in this exhibition has never been bettered ... the deserved claim to be the international forum for the surface coatings industries."

"The exhibition was well attended and seemed to need all of the vast space in the crowded middle periods when so many overseas visitors dominated."

*The British Ink Maker, May 1979*

### Invitations to Exhibit

Invitations to Exhibit, giving details of the various types of exhibition facilities available at OCCA-32 have been despatched, together with application forms, to those companies who have exhibited at previous OCCA Exhibitions, or have requested information for the first time for OCCA-32. Any organisation which has not yet received a copy of the Invitation to Exhibit and wishes to do so, should write to the Director & Secretary at the address on the Contents page.



A view of part of the Queen Mary Suite at the Cunard International Hotel

Completed application forms should be returned to the Director & Secretary of the Association by **30 November 1979**, as the initial allocation of space in the New Exhibition Hall and Queen Mary Suite will then take place. As mentioned earlier, all the rooms on the Mezzanine floor have already been allocated, and those remaining on the third floor will be allocated on a first come, first served basis. Early application is advised.

**Official Guide**

It is intended, as in previous years, to publish the *Official Guide* to the Exhibition several weeks in advance so that it may be sent to visitors to enable them to plan the itinerary for their visits. The *Official Guide* will contain descriptions of all the exhibits together with much other useful information for visitors, such as

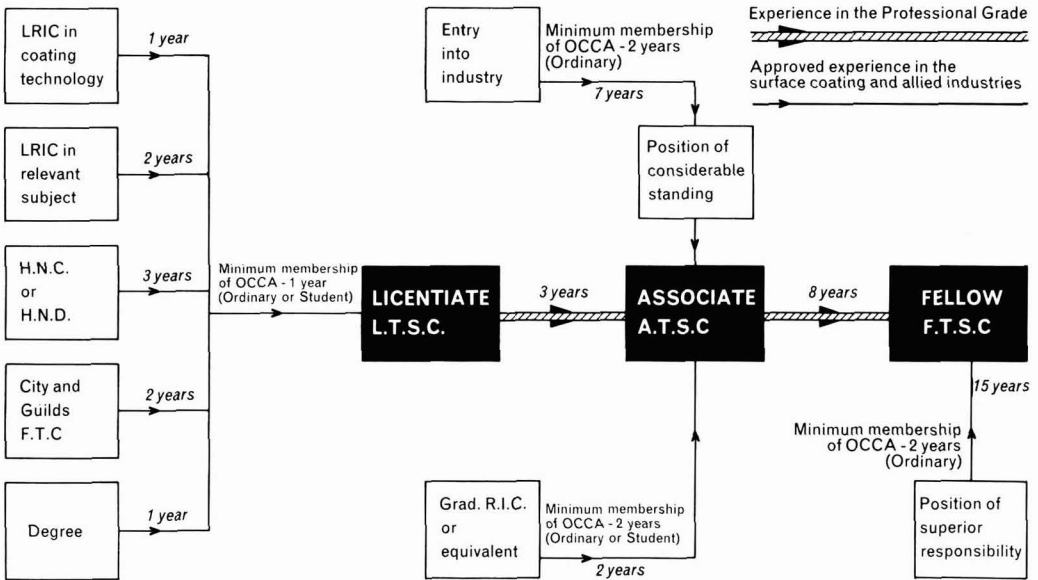
maps of the exhibition areas, details of facilities, travel information and an analysis of the exhibits.

Many thousand copies of the *Official Guide* will be printed and distributed on a world-wide basis. Advertising space will be available in this publication, and details of availability, rates, special positions etc., may be obtained from the Assistant Editor at the address on the Contents page.

## Optional Professional Grade for Ordinary Members

The innovation of the Professional Grade has proved to be most successful, as evidenced by the impressive list of names in the December issue of the *Journal*. For the convenience of potential applicants, a chart indicating different routes to the various grades is shown below.

**Routes to the Professional Grades**



Note: At present there is no restriction on Students up to 21; between 21 and 25 a certificate from the employer or college confirming the course being taken is required.

## Bristol Section

**Annual skittles match**

The annual skittles match between the Birmingham Paint, Varnish and Lacquer Club and the Bristol Section, for the unique Alkyd Cup took place during the summer recess at the Kings Head Inn, Kings Stanley near Stroud, when over 50 members and their ladies attended.

It was unfortunate that the Chairman of the Section, Mr D. N. Fidler, was unable to attend. However, Mrs E. Harper, Vice-Chairman, took over the Chairman's duties at short notice and welcomed the President of the Birmingham Paint, Varnish and Lacquer Club.

The event was much enjoyed by all

present and the Cup was again won by the Birmingham side.

J.R.T.

## Manchester Section

**Brewery visits**

Contrasting sharply with the Section's occasional contact with dry subjects, the two visits provided completely different and very interesting entertainment.

*Visit number 1*

On the evening of 7 June, 24 members

visited Matthew Brown & Co. Ltd, Lion Brewery, Little Harwood, Blackburn, and were introduced to Jim Botur, General Foreman and the guide for the evening.

This is a traditional brewery using hessian bagged malt, which the party sampled, combined with copper mash tuns, wort and hop processing and open fermenting tanks. The intriguing pattern created by the yeast on the surface of the fermenting beer was the subject of much speculation before the party progressed to the filling department. Thorough cleaning of both barrels and kegs coupled with a degree of automation ensures a quality product. Adjoining to their new social club, the party were privileged to sample the full range of beers, lager and stout as well as the traditional pie and peas. Future mention of Blackburn's Heritage will rightly be referred to that excellent bitter brewed by Matthew Brown.

*Visit number 2*

The second visit was to Samesbury Brewery, Preston, on 19 June by 20 members as guests of Whitbread (West Pennines) Ltd. Escorted by Margaret Gorrill of the PRO Department, the group initially enjoyed a rather witty film entitled "I know what I like", featuring Bernard Cribbins in a multi-role acting saga.

In contrast to the first brewery visit, this brewery is computer controlled, constructed almost entirely of stainless steel,

and the associated statistics are mind boggling; this low level brewery occupying 80 acres can produce 400 million pints of beer/lager per year, pays HMG £2 million per month in excise duty, brewing every three hours with three shifts worked by 450 people, and requiring five pints of water to produce each pint of beer.

During the visit the emphasis on hygiene, quality and quantity was well demonstrated, and the tour was concluded by an excellent buffet accompanied by a range of beers and lagers. It was also

learnt that Heineken Lager is brewed with yeast specially imported from Holland, that Helden Brau is the Hero's brew, and that one OBJ with a Gold Label is unofficially known as rocket fuel, a fact that one of the members discovered personally.

To conclude, the thanks of the Section are due to the management of the respective breweries for their invitations and also to Ken Wright of the Manchester Section for the excellent arrangements.

F.B.W.

## Register of Members

---

The following elections to membership have been approved by Council. The Section to which each new Member is attached is given in italics.

**Ordinary Members**

BERRY, MARILYN ERICA, Duluz NZ Ltd, Hutt Park Road, Seaview, Petone, New Zealand. (*Wellington*)

BURWELL, BARRY, 17 Whitby Close, Ainsworth Road, Bury, Lancs. (*Manchester*)

DALZELL, KERRY WAYNE, MSc, Chemistry Division, DSIR, Private Bag, Petone, New Zealand. (*Wellington*)

FOSTER, FRANK, Rigby Taylor Ltd, Paints Division, Garside Street, Bolton, Lancs. (*Manchester*)

McNAUGHTON, ALLAN JOHN, MSc, 16 Leona Way, Paparangi, Wellington, New Zealand. (*Wellington*)

USSHER, DAVID ARLAND, BSc, Polychem (NZ) Ltd, PO Box 9141, Wellington, New Zealand. (*Wellington*)

YAQUB, MOHAMMAD, BSc, Champion Paint Industries Ltd, PO Box 1035, Multan Road, Lahore, Pakistan. (*General Overseas*)

**Associate Members**

MELLOR, JAMES IAN, 15A Tennyson Avenue, Lower Hutt, New Zealand. (*Wellington*)

MURRAY, TERENCE JOSEPH, Silicate & Chemical Industries, PO Box 12062, Jacobs 4026, South Africa. (*Natal*)

ROYLE, ALAN FRANK, Ellis Jones & Co. (Stockport) Ltd, Tiviot Colour Works, Manchester Road, Stockport SK4 1UA. (*Manchester*)

## Forthcoming Events

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Details are given of Association meetings in the United Kingdom and Ireland up to the end of the second month following publication and in other parts of the world up to the end of the third following publication.

**October****Monday 1 October**

*Hull Section:* "Plant and machinery for the processing of oil seed and vegetable oils" by N. Lithgoe of John L. Seaton & Co., at the Humber Bridge Hotel, Barton, South Humberside, commencing at 6.45 p.m.

**Tuesday 2 October**

*West Riding Section:* "The use of titanium dioxide in air drying paints" by J. Clark of BTP Tioxide Ltd, at the Mansion Hotel, Roundhay Park, Leeds 8, commencing at 7.30 p.m.

**Friday 5 October**

*Hull Section:* Annual Dinner Dance, at the Willerby Manor Hotel, Willerby, near Hull. *Details to be announced.*

**Thursday 11 October**

*Midlands Section - Trent Valley Branch:* "Pigment dispersions for solvent based decorative paints" by H. H. Bower and A. Kelly of Ciba-Geigy Ltd, at the Derby Crest Motel, Pastures Hill, Littleover, Derby, commencing at 7.15 p.m.

*Newcastle Section:* "Leather finishing" by G. J. Ward of Rohm & Haas Ltd, in the Students Common Room, St. Mary's College, Elvet Hill Road, Durham, commencing at 6.30 p.m.

*Scottish Section:* "Corrosion" by C. U. Chisholm of Paisley College of Technology, at the Albany Hotel, Glasgow, commencing at 6.15 p.m.

*Thames Valley Section:* *Works visit*, to Pyrene Chemical Services Ltd, Iver, Bucks, commencing at 6.30 p.m.

**Friday 12 October**

*Manchester Section:* "European versus UK test methods for emulsion paints" by J. Legg of Vinyl Products Ltd, at the Manchester Polytechnic, New Administration Building, All Saints, commencing at 6.30 p.m.

**Wednesday 17 October**

*London Section:* "The maintenance and protection against corrosion of North Sea structures" by M. Small of Berger (UK) Ltd. Joint meeting with the London Branch of the Institute of Petroleum, at 61 New Cavendish Street, London W1, commencing at 6.00 p.m.

**Thursday 18 October**

*Midlands Section:* "In-line coat-

ings – Another approach to accelerated drying in print” by G. Gooding of Mander Kidd Ltd, at the Calthorpe Suite, County Cricket Ground, Edgbaston, Birmingham, commencing at 6.30 p.m.

#### Friday 19 October

*Irish Section:* “Printing ink lecture” at the Clarence Hotel, Dublin, commencing at 8.00 p.m. *Details to be announced.*

*London Section: Ladies' Night,* to be held at the Selsdon Park Hotel, Sanderstead, Surrey, commencing at 7.00 for 7.30 p.m.

*Manchester Section:* Annual Dinner Dance, at the Piccadilly Hotel, Manchester. *Details to be announced.*

*Scottish Section – Eastern Branch:* Annual Skittles Match for the Newton Cup, in the Telecom Club, Chesser Avenue, Georgie Road, Edinburgh, commencing at 7.30 p.m.

#### Wednesday 24 October

*Association Reunion Dinner* for past and present members of Council, at the Great Northern Hotel, London N1 at 6.00 p.m. for 7.00 p.m. *Informal dress.*

#### Thursday 25 October

*London Section:* “Preservation, priming, putty and paint” by J. J. Froggatt, at the Rubens Hotel, Buckingham Palace Road, SW1, commencing at 7.00 p.m.

#### Friday 26 October

*Bristol Section:* “Problems of painting at tropical and sub-zero temperatures” by J. R. Taylor, at the Royal Hotel, Bristol, commencing at 7.15 p.m.

*Midlands Section – Trent Valley Branch:* Halloween Buffet & Dance, at the Cross Keys Inn, Turnditch. *Details to be announced.*

### November

#### Thursday 1 November

*Newcastle Section:* “Antifoulings” by J. D. Symonds of International Marine Coatings, in the Students Common Room, St. Mary's College, Elvet Hill Road, Durham, commencing at 6.30 p.m.

#### Monday 5 November

*Hull Section:* “Instrumental colour control in the paint industry” by Miss S. Williams, Director (Applications Department), Instrumental Colour Systems, at the George Hotel, Land of

Green Ginger, Hull, commencing at 6.30 p.m.

#### Tuesday 6 November

*Scottish Section:* “The effect of instrumentation on management” by J. M. Scadlock of J & P Coats UK Ltd. Joint meeting with the Society of Dyers & Colourists, at the North British Hotel, Glasgow, commencing at 7.30 p.m.

*West Riding Section:* “The biology of paint and paint films” by E. Allsop of the University of Aston, at the Mansion Hotel, Roundhay Park, Leeds 8, commencing at 7.30 p.m.

#### Thursday 8 November

*Thames Valley Section:* “The pigmentation of non-polluting coatings” by T. Entwistle of British Titan Products Ltd, at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks, commencing at 6.30 p.m.

#### Friday 9 November

*Irish Section:* Annual Dinner Dance, at the Clarence Hotel, Dublin, commencing at 8.30 p.m.

#### Monday 12 November

*Manchester Section:* “Photography – Do you need help?” by N. Webster of Nicholas Webster Photography Ltd, at the Woodcourt Hotel, Sale, commencing at 6.30 p.m.

#### Wednesday 14 November

*Scottish Section – Eastern Branch:* “The language of colour” by J. Hunter of the Design Department, Scottish College of Textiles, at the Maybury Road House, Maybury Road, Edinburgh, commencing at 7.30 p.m.

#### Thursday 15 November

*Midlands Section:* “Solvent system design” by R. L. Mawer of Shell Chemicals Ltd, at the Calthorpe Suite, County Cricket Ground, Edgbaston, Birmingham, commencing at 6.30 p.m.

#### Wednesday 21 November

*London Section:* “Pigments”. Day meeting at the Thames Polytechnic, Woolwich, SE18, commencing at 10.00 a.m. *Details to be announced.*

*Manchester Section: Students' Lecture,* “Weatherability of surface coatings” by E. Oakley of BTP Ltd, at the Manchester Polytechnic, New Administration Building, All Saints, commencing at 4.30 p.m.

#### Friday 30 November

*Bristol Section: Ladies' Evening.*

“Furs” by D. Bauers of F. K. Bauers of Bristol, at the Royal Hotel, Bristol, commencing at 7.15 p.m.

### December

#### Monday 3 December

*Hull Section:* “Adhesion of surface coatings: Fact and fiction” by M. Wilkinson of Blundell-Permglaze, Decorative Division, at the George Hotel, Land of Green Ginger, Hull, commencing at 6.30 p.m.

#### Tuesday 4 December

*West Riding Section:* “Quality assurance in process industries, with special reference to paint” by D. J. Murray, at the Mansion Hotel, Roundhay Park, Leeds 8, commencing at 7.30 p.m.

#### Wednesday 5 December

*Scottish Section – Eastern Branch:* “Fire and hygiene hazards associated with the surface coatings industry” by W. W. Ashcroft-Hutton and R. U. Khan of the Health & Safety Executive, Edinburgh, at the Murrayfield Hotel, 18 Corstorphine Road, Edinburgh, commencing at 7.30 p.m.

#### Thursday 6 December

*Newcastle Section:* “Setting up a paint company” by J. R. Bourne of Mebon Ltd, at the Students Common Room, St. Mary's College, Elvet Hill Road, Durham, commencing at 6.30 p.m.

*Thames Valley Section:* “Dispersants for emulsion paints” and a film on dispersants by A. S. Doyle of IMC Chemie GmbH, at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks., commencing at 6.30 p.m. for 7.00 p.m.

#### Friday 7 December

*Irish Section:* “Handling of dangerous chemicals” by FICI, at the Clarence Hotel, Dublin, commencing at 8.00 p.m.

#### Thursday 13 December

*Scottish Section:* “100 years of colour chemistry” by I. D. Ratee, School of Colour Chemistry, University of Leeds, at the Albany Hotel, Glasgow, commencing at 6.15 p.m.

#### Friday 14 December

*Manchester Section:* “Matting silicas and their use in UV cured systems” by R. C. Chapman of Joseph Crosfield & Sons Ltd, at the Manchester Polytechnic, New Administration Building, All Saints, commencing at 6.30 p.m.

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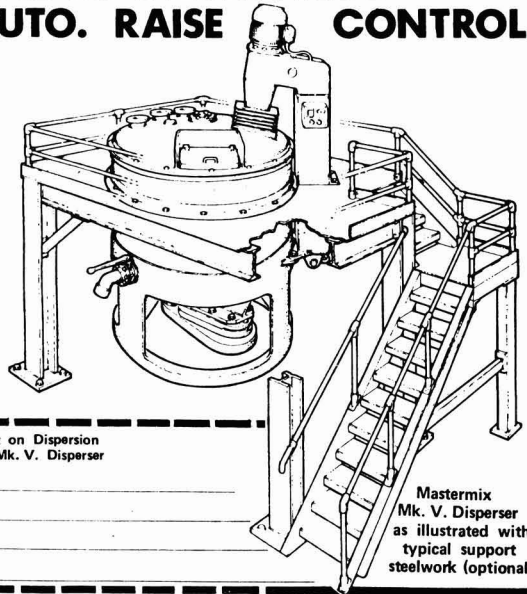
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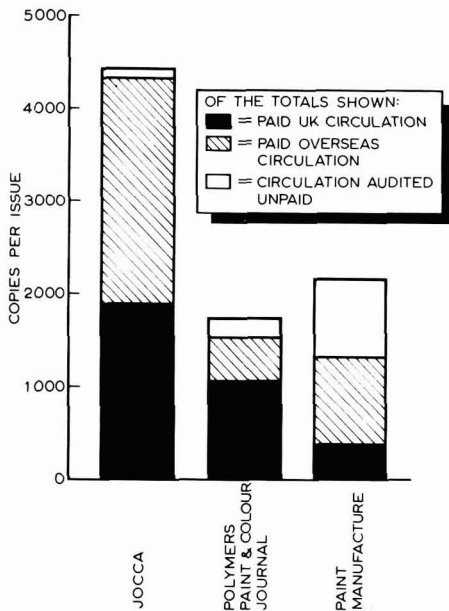
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## SITUATIONS VACANT

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**OCCA-32 EXHIBITION**  
Cunard International Hotel  
London, 13-15 May 1980

## SITUATIONS VACANT

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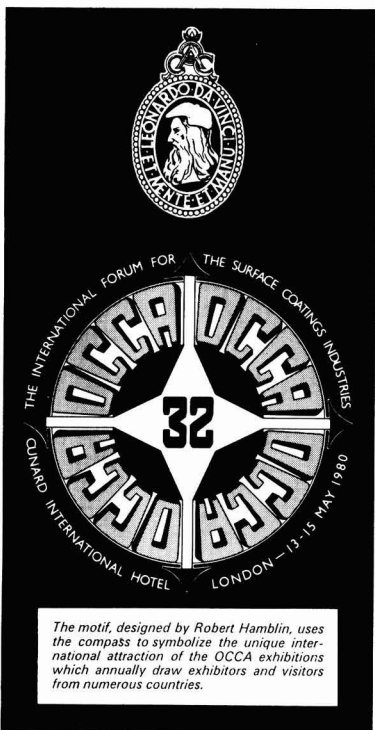
Please write with full details. These will be forwarded direct to our client. List separately any companies to whom your application should not be sent.  
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*This appointment is open to men and women.*

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CLASSIFIED ADVERTISEMENTS



The motif, designed by Robert Hamblin, uses the compass to symbolize the unique international attraction of the OCCCA exhibitions which annually draw exhibitors and visitors from numerous countries.

**32ND ANNUAL EXHIBITION**  
 OF THE  
**OIL & COLOUR CHEMISTS' ASSOCIATION**  
**CUNARD INTERNATIONAL HOTEL**  
**LONDON · 13-15 MAY 1980**

The world's most important international exhibition of raw materials, plant and equipment used in the Paint, Printing Ink, Colour, Adhesives and Allied Industries.

**TUESDAY 13 MAY 09.30 - 17.30**  
**WEDNESDAY 14 MAY 09.30 - 17.30**  
**THURSDAY 15 MAY 09.30 - 17.30**

**ADMISSION FREE**

*Copies of the Invitation to Exhibit and application forms obtainable from the Director & Secretary (Mr. R. H. Hamblin) at the following address:*

**Oil & Colour Chemists' Association,**  
**Priory House, 967 Harrow Road, Wembley, Middlesex,**  
**England, HA0 2SF**  
**Telephone: (01) 908 1086 Telex: 922670 (OCCA Wembley)**

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# OCCA-32 Exhibition

13-15 May 1980 Cunard International Hotel  
Hammersmith, London W6

**Motif:** The motif, designed by Robert Hamblin, uses the compass to symbolize the unique attraction of the OCCA exhibitions which annually draw exhibitors and visitors from numerous countries.

The aim of the Exhibition is the presentation of commercial and technical information relating to raw materials, plant and equipment used in the paint, polymer, printing ink, colour, adhesive and allied industries, both in their manufacture, processing and application.

The Exhibition Committee will be particularly pleased to welcome exhibits from companies relating to the new energy efficient, low-polluting technologies, including powder coatings, high solids coatings, radiation curing, water-based coatings and other developments.



The main part of the Exhibition will be in two sections. The entrance to the Exhibition will be on the ground floor in the new Exhibition Hall, in which exhibitors of heavy machinery, plant and equipment or those wishing to have the traditional style of stand will be situated. On the first floor, additional exhibitors, mainly of raw materials, laboratory equipment or other small exhibits, will be accommodated in the Queen Mary Suite, in which the stands will be of a modular design. The Queen Mary Suite is a large pleasant room which is decorated and carpeted as an integral part of the hotel.

In addition, several suites and rooms will be available on the intermediate Mezzanine floor and third floor for those companies who wish to use that type of facility to exhibit, or to entertain their visitors in addition to their stands in the main halls.

## NEW VENUE AND STYLE



The motif for OCCA 30 used the symbol of a moving indicator on a calendar to emphasise the importance of the continuous dialogue year by year between suppliers and manufacturers.

### THE ANNUAL FOCAL POINT FOR THE SURFACE COATINGS INDUSTRIES

The Exhibition Committee has decided to move the venue of the Exhibition from Alexandra Palace in north London, to the more centrally sited Cunard International Hotel as it is felt that this modern hotel will offer Exhibitors a greater choice of types of exhibiting facilities, as well as the improved services to both exhibitors and visitors which a first class hotel can offer.

Admission to the Exhibition will be free, and visitors will be asked to complete registration cards which will be available in advance from the Association with copies of the *Official Guide*. Copies of the *Official Guide* will be charged at £1.50 each, and both registration cards and copies of the *Official Guide* will also be available at the Exhibition.

The Exhibition provides an ideal opportunity for organisations to display and discuss their products and services to a wide spectrum of visitors from all over the world.

Organisations wishing to receive further details should contact the Director & Secretary, Mr. R. H. Hamblin, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, England (Tel: 01-908 1086, Telex: 922670 OCCA G).



The motif for OCCA 31 emphasised the unique aspect of the OCCA Exhibitions, which annually provide an international focal point for the surface coatings industries.



The motif for OCCA 28 emphasised that the target for 1976 was London where all the Exhibitions have been held, regularly attracting both exhibitors and visitors from over fifty countries.



In 1977 the motif for OCCA 29 used inward pointing arrows to show the many places from which people came to the Exhibition, and these arrows formed outward pointing arrows to show the subsequent spreading of knowledge.