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## SURFEX 86

14th-15th May 1986

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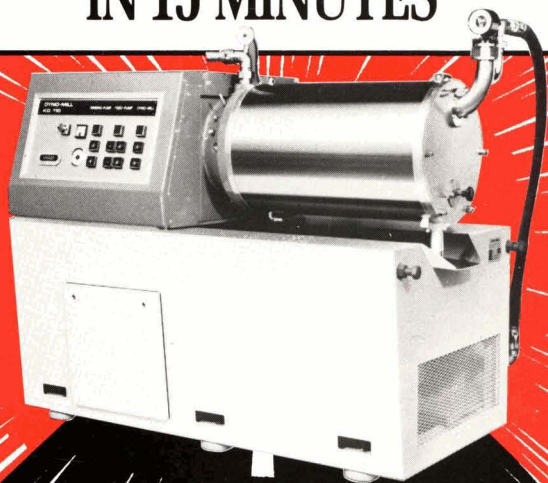
### In this issue:

- Parameters controlling colour acceptance in latex paints
  - Paint adhesion to galvanised steel surfaces, Part I: Effects of binder and pigments
  - Non-phthalic alkyd resins based on maleopimaric acid
- ✉ Wet Adhesion

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## OIL AND COLOUR CHEMISTS' ASSOCIATION

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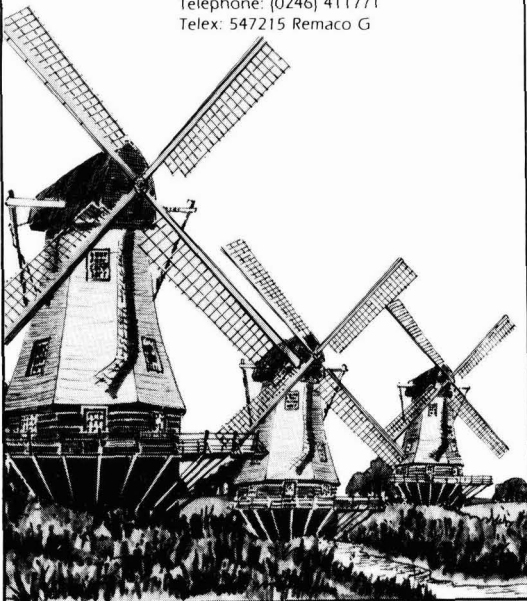


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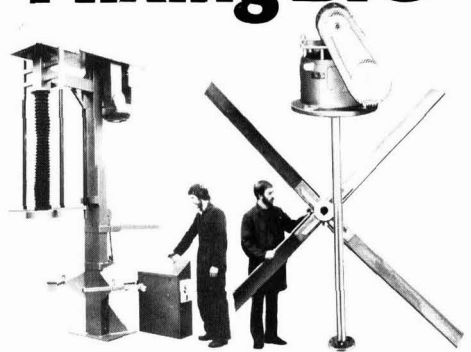
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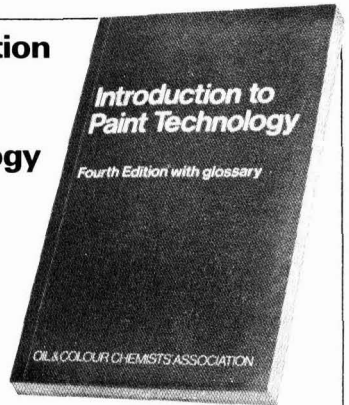


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# Parameters controlling colour acceptance in latex paints

H. G. Stephen

48 Broadgully Road, Diamond Creek, Victoria 3089, Australia

## Summary

This paper follows part I which was presented at FATIPEC, Lugano, 1984.

The two papers, taken together, show that improved Universal Colorants may be formulated so that they will produce minimum energy level differentials, leading to accurate colour matches free from film defects, when added to decorative paints. The paints to be tinted must also be formulated for optimum electrostatic and thermodynamic properties, to normalise the effect of the entropy level of the entering colorant.

From the foregoing it can be seen that no magic single ingredient can be added to any particular paint formulation to give acceptable appearance, with a range of Universal Colorants. It is possible, with refined formulation techniques, to develop higher standards of performance than is currently available with commercial colorants.

## Introduction

In a Paper<sup>2</sup> delivered to the FATIPEC XIV Congress, Lugano, September 1984, it was shown that for optimum colour acceptance it is necessary to use an alkyd resin containing a high percentage of high molecular weight polymer as a basic vehicle. Universal colorants then enter such enamel systems under conditions of controlled co-flocculation influenced by:

1. The HB/SP (Hydrogen Bonding/Solubility Parameters) values of the base pigment<sup>2</sup> utilised in the enamel.
2. The HB/SP values of the alkyd and the solvent system.
3. The entropy state of the entering colorant.
4. The surfactant, and its concentration, in relation to the above three controls. In enamel systems the required surfactant is a flocculant by function.
5. Time of storage after colorant addition.

This present paper shows that, when the same colorants enter latex systems they must do so under conditions of co-dispersion if good acceptance is to occur.

This acceptance is influenced by:

1. The HB/SP values of the base pigment utilised in the latex.
2. The HB/SP values of the water phase and the latex solids taken together as one entropy state.
3. The entropy state of the entering colorant.
4. The surfactant and dispersant, and their concentrations, in relation to the above three controls. In the latex

systems both surfactant and dispersants are dispersing agents by function.

5. Time of storage after colorant addition.

Data is also included on the effect of outdoor weathering in Melbourne, on both the alkyd and emulsion systems.

## Experimental

The initial approach utilised was to optimise a PVA homopolymer latex formulation for colorant acceptance, employing the approach indicated by Stephen<sup>1</sup> and Asbeck<sup>3</sup>, by use of the correct surfactant and dispersant on an HLB structure and quantity basis. The optimum point was determined for one high dispersion grade of r-TiO<sub>2</sub> for:

- (i) Rheological behaviour - minimum Thixotropic Index.
- (ii) Dispersion standard - maximum gloss.
- (iii) Minimum  $\Delta E$  value, determined and expressed by the use of the Hunter Tri-Stimulus Colorimeter, as employed in the previous paper<sup>2</sup>.
- (iv) Contrast Ratio.

The optimum content for the designated surfactant was determined using a previously known optimum for the dispersant. Purely coincidentally, the energy level of representative of 100 per cent of the commercially available acrylic emulsion is identical to the particular pva homopolymer evaluated. Therefore the derived data also applies to these acrylic latexes, (see Figure 1) for the particular grade of r-TiO<sub>2</sub> selected "C".

This data appears in Table 1 (Surfactant) and Table 2 (Dispersant) above, utilising r-TiO<sub>2</sub> "C"<sup>1</sup>, HB value 8.5, HLB requirement 17, as derived by Stephen<sup>1</sup>. Further, Eade<sup>4</sup> draws attention to the different optimum in gloss, hiding and colour acceptance deriving from surfactant and dispersants. It is evident from these two tables that the surfactant exercises some degree of control over the  $\Delta E$  response, where as the dispersant exercises greater influence over gloss levels. Proceeding on a basis of data available to the average formulator, the effect of particle size of any given latex on the value of  $\Delta E$  was then examined, as given in Table 3.

All data was developed in a gloss latex system in order to examine more fully the control exercised by the nature of the latex itself. Inert extenders were excluded in any case, on the basis of Simpson's<sup>5</sup> findings in relation to their effect on the Contrast Ratio and Flocculation Gradient. In the particular systems utilised no added thickener was necessary to achieve end viscosity, but Blake<sup>6</sup> states that variation in the molecular weight of thickeners does not influence colour acceptance. All  $\Delta E$  values were obtained

Table 1.

Response to surfactant

Rx	Surfactant %	Viscosity	TI	Gloss 60%	C. Ratio	dCR	E <sub>3</sub> Blue	E <sub>3</sub> RedOx.
A	0.5	8400/1680	5.0	69	0.9545		1.640	0.781
B	1.0	5500/1260	4.36	70	0.9535	0.001	1.009	0.447
C	1.5	5650/1320	4.28	72	0.9515	0.002	0.806	0.538
D	2.0	6280/1370	4.58	71	0.9515	0.000	1.470	0.608

When optimum surfactant level had been determined the optimum dispersant was then re-determined.

Data: TiO<sub>2</sub>C HB 8.5 40 mol.; NP-Eth. Ox. Surf.; HLB value 17.6.

Table 2.

Response to dispersant

Rx	Dispersant (%)	Viscosity	TI	Gloss-Orig.	Gloss 3 days	Contrast Ratio	E <sub>3</sub>	dCR. Opt
E	0.2	46.000/7150	6.43	60	45.7	0.9515	2.083	0.003
F	0.4	13.750/2560	5.37	54.5	37.2	0.9485	1.664	0.0015
G	0.6	7.900/1850	4.27	53.0	37.6	0.9470	1.364	
H	0.8	6.300/1650	3.82	53.0	37.8	0.9465	1.319	0.0005
J	1.0	6.150/1560	3.94	47.0	36.4	0.9435	1.304	0.003

Data: TiO<sub>2</sub>C HB 8.5 HLB value 17.6 40 mol. NP-Eth. Ox. Surf. sodium polyacrylate.

Table 3.

Response to particle size of the emulsion

Rx	Latex particle size	E <sub>3</sub> Blue	Comparative state
K	Medium fine, coarse bias	0.447	Most flocculent
L	Fine	0.806	
M	Very fine, coarse bias	1.005	↓ Most disperse
N	Extremely fine	1.204	

Data: TiO<sub>2</sub>C, 1.45% 40 mol.; NP-Eth. Ox.; 0.8% sodium polyacrylate.

utilising Blake's<sup>6</sup> procedure, but using a brush in place of a roller.

Once optimised at 0.18 kg, r-TiO<sub>2</sub>/litre (standard mid tone base concentration), all the paints were tinted with 5

per cent volume/volume addition of colorant. One hour after this was added, both viscosity and thixotropic index were determined, together with the preparation of a brush out on sealed Leneta card. The paints were then matured for three days and the above procedure repeated. This

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yields the thixotropic index, gloss and  $\Delta E$  changes for this period, as suggested by Siddic<sup>7</sup> and confirmed in over 600 tests in this work. Later work shows that 15 minutes Red Devil shaking is equivalent to a three-day maturing period.

These three differentials taken together indicate the entropy changes occurring due to the addition of the colorant which, in turn, indicates the degree of colorant acceptance and further gives the key to the optimum formulation of the colorants.

## Discussion

The previous paper<sup>2</sup> drew attention to the fact that colorant acceptance into enamels is maximised when alkyd molecular weight is high; this is closely paralleled in latex systems which are formulated and processed to yield polymers of high molecular weight *per se*.

However, these latex polymers are dispersed in a highly polar external phase, water HB 8.5/23 SP, whereas the optimised alkyd system is dispersed in a non-polar solvent system ca HB 2/5 SP. This is the fundamental pointer to the entropy state required in the colorant.

An earlier paper<sup>2</sup> showed that HB/SP of the alkyd solids were an influential factor, which will also be demonstrated for the latex polymer.

Homopolymer vinyl acetate latexes may be prepared in a surfactant starved system, due to the relatively high solubility of vinyl acetate in water. When vinyl acetate copolymers are prepared extra surfactant must be added, in order to emulsify the comonomer to allow it to undergo micelle formation to solubilise the comonomer. When non-ionic surfactants are used, concentration is normally 3-6 per cent on the monomer level, whereas anionics may be as low as 0.5 per cent (or even lower) depending on comonomer content, while at the same time producing much smaller particles than non-ionic systems. The source of the data in Table 3 is thus evident. The more hydrophobic the disperse phase in the latex, the more sensitive it will be in terms of  $\Delta E$  and gloss to deviation from optimum HLB values in the latex, in the formulated paint and upon addition of the colorant, as shown in Figure 1.

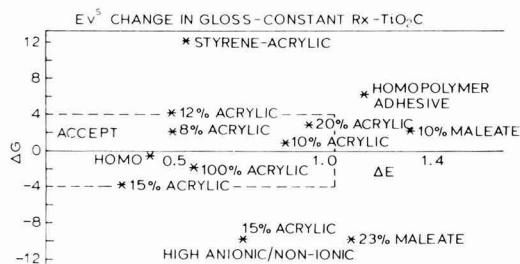


Figure 1.

This is due to the fall in entropy level when vinyl acetate copolymerises with acrylic monomers, as the HB/SP values for vinyl acetate are higher than those for the acrylic monomers employed. It is known that acrylic acid confers

stability on copolymer latexes since it has HB/SP values somewhat higher than vinyl acetate and acrylates; thus 88 per cent; VAM/10 per cent 2-ethyl hexyl acrylate/2 per cent acrylic acid has the same entropy level as vinyl acetate monomer; however, the particle size of the copolymer will be smaller, yielding slightly higher  $\Delta E$  value (Figure 1).

These values hold for the polymer, just as for the monomer, as Burrell<sup>8</sup> states that the particular polymerisation being by addition, the polymer merely increases in molecular weight with no condensation reactions occurring to change the basic chemical structure.

When 100 per cent acrylic or styrene-acrylic latexes are considered, either anionics of very high polarity are used in small percentage, or the HLB of the non-ionic has to be higher, in order to emulsify the now low entropy level monomer, e.g. styrene HB 2.5/9.3 SP. Either way, the latexes finally have finer particle size giving the results as shown in Table 3.

Paper<sup>2</sup> showed that the nature of the alkyd solids has to be considered in conjunction with its solvents system. Latexes must be treated in the same manner, as colour acceptance properties are influenced by HB/SP values of both the internal and the external phases. Thus, it is imperative to be able to assess the entropy level of each phase, and, via the volume solids content, to calculate the HB/SP values for the bulk latex. A 55 per cent NV VAM latex calculates to 50 per cent volume solids—thus the HB/SP level of the bulk latex is the mean value of those of the internal and external phases. It is this state, which, in turn, dictates the energy level at which the colorant must be formulated, in order to attempt to obtain the same  $\Delta E$  and colour, when it is added, either to a latex or an enamel. If the surfactant/dispersant values and levels in the latex paint are not optimum values, then all the faults such as high  $\Delta E$ , colour drift, flooding, striation, and gloss variations, appear in proportion to the inaccuracies in the base formulation. These faults are observed everyday in the surface coatings industry.

When the HB/SP values of the colorant are off-optimum, violent changes can occur in strength and colour cast, see Table 4.

This can be shown to induce quite marked variations in exposure performance.

Furthermore, Burrell<sup>8</sup> infers that for the colorant to be compatible (and, hence to disperse) in the water phase, its HB value must be within one HB unit of that of the water phase of a latex paint, i.e. approximately 7.5-9.5. Now, if it is to disperse in the water phase of the bulk latex, it must have an SP value close to that of the bulk latex — but it is also required to enter the solvent phase of an enamel and flocculate — obviously then, the total energy level of the colorant must be close to the mid-point between those of the bulk latex system, and the bulk alkyd vehicle system. It is this compromise, or lack of it, that leads to the common faults encountered in decorative paints and to variable  $\Delta E$  values, particularly when colorants enter off-optimum paints of any type.

As the comonomer and HLB of the surfactant system in myriad practical latexes vary so widely, the entropy differentials are as numerous as the formulated paints,

Table 4.

Effect of tinter energy level variation  
(TiO<sub>2</sub> C optimised, Phthalo blue)

Tinter	Sol. Parameter	HB Value	$\Delta E_3$ Latex	$\Delta E_3$ Enl.	Status	Change in enamel appearance
A	Sl. Low	V. Low	0.714	1.516	Reject	Dirty col. gone
B	Optimum	Optimum	0.548	0.700	Accept	NIL
C	V. High	Optimum	0.346	3.215	Reject	Striation then heavy flood
D	Commercial A	—	1.364	0.426	Reject	(?) NIL-saves
E	Sl. High	Low	0.316	2.012	Reject	Sl. striation, Sl. flood
F	High	Optimum	1.122	0.245	Reject	(?) NIL-saves
G	High	Sl. Low	0.678	9.339	Reject	Strong whiteflood col. brushed up
H	Commercial B	—	1.068	0.927	Just accept	Sl. faults, accept
J	Refined Opt.	Optimum	0.447	0.361	" "	NIL- 4 sectors as I

Table 5.

Equalisation of dispersants - PVA Homopolymer

TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	HB	$\Delta E_3$ Blue	Surf. NP-Eth. Ox	PLUS Sod. Poly Acrylate	$\Delta_2 E$	$\Delta_3 E$
A	Low	High	2.0	1.000	2.2% 100 mol.	2.3% w/w	0.561	A-D
D	Med.	Med.	5.5	1.000	1.8% 40 mol.	1.6% w/w	0.436	1.00
C	High	Low	8.5	1.000	1.45% 40 mol.	0.8% w/w		

hence  $\Delta E$  values obtained (accompanied by relevant application faults), are also just as numerous. The approach to normalise  $\Delta E$  is given in Table 5.

Twenty years of observation of latex paint formulae deficient, or incorrect, in both surfactant and dispersant, throughout the manufacturing industry, have shown this to be true. Careless, or uninformed replacement of one grade of rTiO<sub>2</sub> by another, takes place every day — contrast, rTiO<sub>2</sub> "A" heavy silica coated with HB 2/6 SP requiring nonylphenol — 100 mole ethoxylate surfactant, as against rTiO<sub>2</sub> "C" heavy alumina coated at HB 8.5/18 SP requiring nonylphenol — 40 mols ethoxylate surfactant for optimum dispersion in the water phase. If the colorant performance can be de-optimised by HB 1/1 SP variation (as given in Table 4) in the colorant which is added at 5 per cent volume/volume maximum, consider the effect of 6 per cent volume TiO<sub>2</sub> contribution at HB 6.5/13 SP differential, on the  $\Delta E$  value after the colorant addition — the TiO<sub>2</sub> contribution swamps that of the colorant and appears as such. A further common practice is to evaluate a new latex (the knowledge of which is limited to the date passed on by its manufacturer) by using it on a straight solids

replacement basis in a standard formulation applicable to the currently used products. Close consideration of Burrell's approach<sup>8</sup> to compatibility and Table 3, will show that for an acceptably equivalent  $\Delta E$  performance to be obtained from the new latex its particle size distribution must be closely similar, and it must meet the requirement  $\Sigma \Delta HB + \Delta SP > 0.1$  to the control bulk latex, with the further inference that if  $\Sigma$  is negative the new formulation will show a tendency to agglomerate, whereas, if  $\Sigma$  is positive the new formulation will show a tendency to become more disperse than the control paint, with consequent effect on colour cast and  $\Delta E$  value in each case, let alone flow, gloss, etc. This data appears in Table 6.

While B, C, and D are acceptable between themselves, they are certainly not acceptable if A is taken as the control for the other three formulae. If such small changes in an homologous series of vinyl acetate copolymers produce these variations in  $\Delta E$ , major changes between latex and ritanita types greatly magnify and extend the faults which can appear. If we evaluate the paint formulae given in Table 5, we obtain for the scrubability value the data given in Table 7.



Table 6.

## Effect of comonomer ratio

PVA/Acrylic homologous series TiO<sub>2</sub>C Constant Rx

Latex	Type	Energy Δ	L	a	b	Visual	ΔE <sub>3</sub>	Gloss	Total Effect
A	Homopolymer	0	68.4	-8.6	-31.8	Control	0.412	0.0	Acceptable
B	10% Comonomer	-0.10	71.19	-8.1	-28.1	Deeper	0.872	4.4	Fair
C	15% Comonomer	-0.15	71.6	-8.3	-28.5	Dirtier	0.961	-3.1	
D	20% Comonomer	-0.20	70.6	-8.4	-29.5	Redder	0.961	2.3	

Table 7.

## Scrub test (ASTM Method)

Exp.	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	HB/SP	Surf. (%)	Disper- sant (%)	ΔE <sub>3</sub> Bl	Scrubs	Latex type
1566	A	Low	High	2/6	2.2	2.3	1,000	1098	Homo VAM
1567	A	Low	High	2/6	2.2	2.3	0.538	720	Styrene Acr.
1569	D	Med.	Med.	5.5/12	1.8	1.6	1,000	720	Homo VAM
1570	C	High	Low	8.5/18	1.45	0.8	1,000	1209	Homo VAM

Comparing 1566, 1569, 1570, it is obvious that the nature, and order, of the coatings are exercising far more influence in the scrub result than the surfactant/dispersant, which is massive in 1566. The poor result in 1567 probably derives from the low ΔE - more than sufficient surfactant/dispersant is present in the S/A latex than is needed. This leads to the thought that lack of scrub probably occurs when incorrect TiO<sub>2</sub> is coupled to irrelevant latex — similarly, how can an incorrect HLB surfactant orient to and be absorbed by an opposed HLB of TiO<sub>2</sub>. Both flocculation and consequent low scrub values must obtain in these conditions, due to the surfactant being free in the water phase and not absorbed to the pigment.

In nature, like prefers like. This author<sup>1</sup> draws attention to the fact that for good dispersion the HB value of pigment and vehicle must obey Burrell's<sup>8</sup> HB concepts. Observe experiments 1566 and 1567 — the low polar TiO<sub>2</sub> matched to the far lower polar styrene-acrylic latex yields far lower ΔE values as given in Table 8.

In the latex paint (in the can) we have internal and external phases. The data in Table 5, shows that we must add a large amount of highly polar dispersant (HB 100/SP 200) in order to disperse the non-polar TiO<sub>2</sub> "A" and proportionally little to disperse the highly polar TiO<sub>2</sub> "C" in the external phase, water. However, as the paint dries

this external phase disappears and the TiO<sub>2</sub> will agglomerate and flocculate depending on the conditions of its environment, namely the concentration and HLB of the surfactant, and the concentration of the dispersant. If the HB/SP of the TiO<sub>2</sub> approximate to those of the now (waterless) previous internal (non-continuous) phase, then flocculation can be expected to be at minimum, promoting superior gloss and colour acceptance. If the HLB of the surfactant and/or HB of the TiO<sub>2</sub> are opposed to those of the polymer then gloss falls, TiO<sub>2</sub> flocculates, and ΔE rises. The characteristic flat white overveiled colour appears. In experiment 1566 "A" TiO<sub>2</sub> at 2 HB/SP 6 encounters (dry) latex solids at 6.3 HB/SP 9.3 and ΣΔHB + ΔSP is +7.6; whereas in experiment 1567 the same TiO<sub>2</sub> encounters solids at 4.1 HB/SP 9.3 and Σ is -5.4; thus, the low polar TiO<sub>2</sub> "A" (accompanied by a large aliquot of surfactant/dispersant) flocculates less when encountering the low polar styrene/acrylic solids, than when encountering more highly polar homopolymer vinyl acetate solids, thus yielding a lower ΔE. The opposite effect will occur to a greater extent as Σ = -13.1 when the high dispersion high polar grade of TiO<sub>2</sub> "C", (much vaunted, correctly, for its ease of water-phase dispersion) accompanied by far lower surfactant/dispersant, attempts to enter low polar styrene-acrylic (dry) latex film. A guide for selection appears in Table 8.

Table 8.

TiO<sub>2</sub> — Latex monomer co-relation

Monomer	HB/SP	TiO <sub>2</sub>	HB/SP	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MTB gloss	Surf. HLB	Dispersant (%)
Vinyl chloride	2.4/7.0	A	2/6	Low	High	50%	5	2.8
Styrene	2.5/9.3	A	2/6	Low	High			
Butyl Acrylate	5.5/9.3	D	5.5/12	Med.	Med.	70%	17	0.8
Methyl Methacrylate	5.5/8.8	D	5.5/12	Med.	Med.			
Vinyl Acetate	6.3/9.2	D	5.5/12	Med.	Med.	11	11	1.8
Acrylic Acid	8.5/12	C	8.5/18	High	Low			
2-pyrrolidone	8.5/14.7	C	8.5/18	High	Low			

Other grades of r-TiO<sub>2</sub> lie between each of the above 3 TiO<sub>2</sub>'s, allowing matching of a particular TiO<sub>2</sub> grade to a particular copolymer latex for optimum performance. Similarly, Table 5 may be interpolated to suit the selected TiO<sub>2</sub> to derive the required surfactant/dispersant content. It should be noted that only in the higher polarity latexes is the point of maximum gloss also the point of maximum colour acceptance — these diverge further as latex polarity falls, and require the addition of ever increasing amounts of dispersant to offset the latex polarity fall. Further to this, if the HB value of the coloured pigment in a given Universal Stainer is the same as that of the (dry) latex film which it enters, then the strength development of the Stainer will be at a maximum simultaneously to purest tone development. As the HB of the colour pigment moves away from this optimum, its tinting strength falls, and the tone becomes dirtier in ratio to ΔHB/ASP. This accounts for different responses between individual tinters when a colorant colour range is added to one particular latex formula, and why additives appear to be specific to particular colours.

The colorant has exactly the same requirement, and if ΣΔE is required to be so small, very accurate formulation to obtain the correct entropy level in the colorant is required. When the entropy level of the colorant is too low it will attempt to enter the internal polymer phase, rather than the external water-phase — it thus precipitates the lower polar polymer. This can be readily demonstrated. Similarly, if the surfactant/dispersant level of the formulated paint is not at the correct entropy level, effects such as floatation, flooding striation, and colour difference on touch-up, appear. When the entropy level is too high in either paint or colorant, the rTiO<sub>2</sub> "C" floods up, as the total system moves up towards the entropy level value of "C", which lies above the optimum energy level required by the ideal latex tint base white.

However, these effects tend to disappear as the entropy level of the colorant and latex paint approach each other — in fact, if the entropy level of the colorant equals that of the optimally formulated latex paint ΔE = 0. This situation can be easily attained with high HB/SP colorants, such as red and yellow oxides with HB values of 8.5 and 9.5 respectively, by the use of a controlled amount of flocculant in the universal tinter. Middle range HB value pigments such as Phthalocyanine Blue, Fast Red, and Lamp Black,

require close formulation balance, while low HB value pigments such as Permanent Yellows must be dispersed with enough anionic surfactant to raise their entropy level to where they can satisfactorily enter the water phase and give sufficiently low ΔE values after entry.

*The 2nd law of Thermodynamics states that:*

- 1 The more ordered the state of the system, the less freedom there is in realising that state. (Get the colorant energy level correct and add to optimised energy level paints if ΔE is to be low.)
2. When a spontaneous process occurs in an isolated system, that system undergoes a change which will take it to the state of maximum probability that can be achieved for the finite process. (Source of film faults.)

This implies that ideal colorants would enter enamels and latex such that both systems should tend to zero energy difference. It can now be seen that the value of ΔE (and accompanying film defects) is a measure of the degree of success in attaining this state, confirming Sorensen's<sup>9</sup> claim that true universal tinters are an impossibility.

*The 3rd law of Thermodynamics states that:*

The Gibbs free-energy change for a process is determined, by the chemical potentials of the species involved. Chemical potential is an intensive property, and for a given chemical species in a given phase, it depends upon the concentration of that species in that phase. The chemical potential μ (i) of component i in a given phase having a specified composition is the Gibb's free-energy which each mole of a substance i contributed to the total free energy of that phase at the specified temperature and total pressure of the system.

To achieve ΔE → 0, i.e. Gibbs free-energy → 0, in a latex system an ideal colorant must enter a latex system formulated to precisely the same energy level as the colorant. This is possible with red and yellow iron oxides, but not with other colours. If not, the value of ΔE increases as the free-energy of the system varies from this level. However, if the colorants were required to enter only latex,

but not enamel systems, the ideal energy state is merely a matter of calculation.

This latter latex energy level in the colorant produces chaos when added to an enamel system, so a median energy level between the latex and enamel systems must be formulated into the colorant if the  $\Delta E$  values of the two systems are to be somewhat similar, and, of necessity, not minimal, but acceptable. By refined techniques the value of  $\Delta E$  can be brought well under 0.5 as given in Table 9. At  $\Delta E = 0.5$ , the colour cannot be tinted closer when viewed by eye.

Table 9.

*TiO<sub>2</sub>C Optimised enamel<sup>2</sup> — Refined tinters*

Colour	Comm'l A	Comm'l B	Comm'l C	Refined (Enl).	Ref. (Latex)	
Perm. Yellow	1.001	1.497	0.606	0.416	1.016	—
Fast Red	1.318	0.568	—	0.414	0.690	
Phthalo Blue	1.149	1.023	0.652	0.241	0.447	
Lamp Black	0.388	0.325	—	0.527	0.200	
Red Oxide	0.370	0.558	0.687	0.362	0.346	
Yellow Oxide	0.880	0.592	—	0.364	0.435	
Average 6 colours	0.851	0.761	0.648	0.387	0.522	0.432
Result:	$\Delta E$ High, Non-uniform visible lack of match		$\Delta E$ Low, uniform acceptable as match to high standard			

**Conclusion**

In the final analysis, when using universal colorants, it is evident that if  $\Delta E$  is to be low and the film free from defects, then the energy levels of the particular grade of titanium dioxide and the total vehicle employed should be equal.

If the titanium dioxide remains at a higher energy level than the rest of the formulation all the familiar application defects appear in direct proportion to the energy level difference.

In solvent borne alkyd enamels, conventional approaches to formulation produce the above defect condition in most enamels. Thus, most enamel formula will require the addition of the flocculant to reduce the overall energy level to that required for any particular grade of titanium dioxide.

In latex systems, energy levels are much more variable than in alkyd systems, being in general higher than those of decorative alkyds. In some cases the energy levels of the titanium dioxides lie below those of the latex (dry) polymer into which they are to be dispersed. This formula situation then requires large amounts of a dispersant to raise the energy level of such titania to that of the latex polymer in order to yield low values of  $\Delta E$ .

Optimum systems derive when the HB/SP values of the surfactant, pigment, and polymer, can be brought into close proximity, as given by Stephen<sup>1</sup>.

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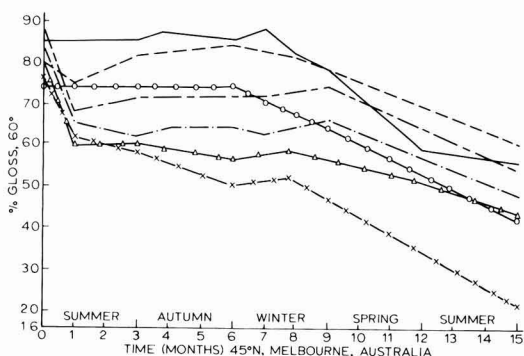
**References**

1. Stephen, H. G., *JOCCA*, 1982, **65**, 191.
2. Stephen, H. G., *FATIPEC*, 1984, Lugano, Paper 88.
3. Asbeck, W., *JPT*, 1977, **59** (635).
4. Eade, C., *Victorian OCCA*, 1983, May meeting.
5. Simpson, L., and Rutherford, D., *FATIPEC*, 1982, Liege.
6. Blake, E., *JPT*, 1983, **55**, 701.
7. Siddle, G., *OCCA*, 1980, Proc. & News 13.
8. Burrell, H. *Ind. Eng. Chem.*, 1954, **46**, 2233; *Off. Dig.*, 1955, **27**, 369, 726, *Off. Dig.*, 1957, **29**, 394, 1159.
9. Sorensen, P., *JPT*, 1975, **47**, 602, 31.
10. Hansen, C. M., 1967, **39**, 511, 505.

**Addendum - Outdoor Weathering**

**Recent exposure results**

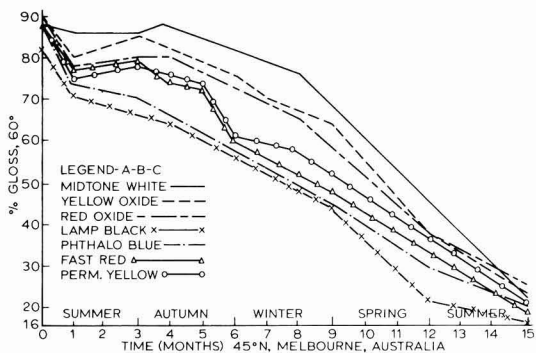
*Exposure Plot "A"* shows data for TiO<sub>2</sub> "A" (high silica coated high chalk resistant grade) of low energy level at HB2/SP6, requiring no lecithin to give sufficiently low values for  $\Delta E$  after tinting with universal colorants. The thixotropic index shows this to be the most flocculent system studied, yielding very good gloss retention on exposure.



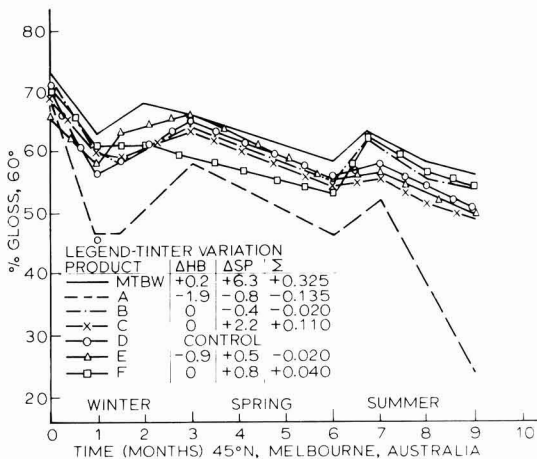
**Exposure plot A. Commercial Colorant B. TiO<sub>2</sub> A no lecithin.**

*Exposure Plot "B"* shows data for TiO<sub>2</sub> "C" (high alumina coated, high dispersion grade) of high energy level at HB 8.5/SP 18, requiring 5 per cent lecithin to give equal  $\Delta E$  values to "A" above and showing much poorer gloss retention than the "A" series.

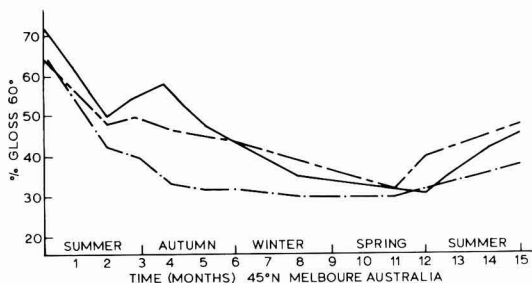




Exposure plot B. Commercial colorant B.  $\text{TiO}_2$  and 5% lecithin.



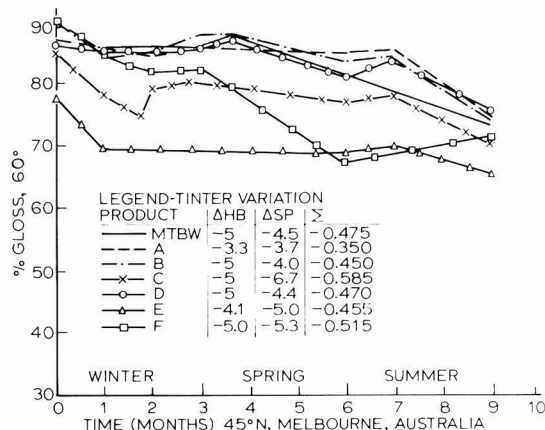
Exposure plot D. Effect of tinter energy level optimised gloss latex  $\text{TiO}_2$  C phthalo blue tinter.



Exposure plot C. Gloss latex, optium E.  $\text{TiO}_2$  C.

All colour panels were tinted with 5 per cent vol/vol addition of colorant and all tint bases carried 0.18kg  $\text{TiO}_2$ /litre.

The results are so different as not to need comment except in the light of the nature of the colorants — the degree of gloss retention is directly related to the degree of flocculation in the tinter as well as to the base tint white itself, as shown in Addendum Table 1.



Exposure plot E. Effect of tinter energy level optimised gloss enamel  $\text{TiO}_2$  C phthalo blue tinter.

Addendum Table 1

Tinter	HB/SP of Pigment	Cationic added flocculant	Electrostatic nature
Yellow Oxide	9.5:18	Very high	Highly Cationic
Red Oxide	8.5:16.5	High	Cationic
Lamp Black	6:12	Medium	Slightly Cationic
Phthalo Blue	5.5:10.5	Slight	V. Slightly Cationic
Fast Red	4:8.5	Very Slight	O.V. Slightly Cat.
Perm Yellow	1.5:6	Anionic added	Anionic

Note that the gloss retention is directly related to the HB/SP, flocculence and electrostatic nature of the tinter except for Perm Yellow which has to be raised in energy level to both disperse in latex and to co-flocculate in an enamel. Lamp Black is erratic due to mis-formulation of the surfactant system.

In particular, plot "A" commences to suggest that the best durability may rest in low energy, flocculent systems, quite contrary to the axiomatic "highly disperse systems are required for best durability".

Note the gloss retention relationship between the colourants is basically similar in both systems.

Exposure Plot "C" once again shows the advantage in gloss retention for the more flocculent red oxide tinter compared to the more disperse phthalocyanine blue tinter when used in latex.

Exposure Plot "D" (gloss latex system) and "E" (gloss enamel system) clearly indicated the necessity to formulate the colorants at fixed energy levels with HB/SP values falling in the region delineated by Burrell<sup>8</sup>, Hansen, Wu<sup>10</sup> Stephen<sup>1,2,3</sup>.

Colorant "A" was formulated to accept easily into enamels, but precipitates latex polymers on addition; colorant "C" was formulated outside an upper limit of SP value (as given in Wu's<sup>10</sup> parallel statement for polymer-solvent relationship, quite independently) for acceptance - the results disqualify both A and C colorants. Colorants B, D and F are thus seen to offer the optimum  $\Delta E$  values and

minimum exposure gloss differentials — all are formulated at the minimum HB value required by Burrell for compatibility in the water phase of latex paints and at the SP value required for co-flocculation into the enamel.

When the value of  $\Sigma \Delta BH + \Delta SP$  is calculated for entry into an optimum latex system we have:


B $\Sigma - 0.020$	$\Delta E 0.361$	$\Sigma \rightarrow 0$
D $\Sigma 0$	$\Delta E 0.385$	Co. Dispersion
F $\Sigma + 0.40$	$\Delta E 0.316$	

and into an optimum enamel system we have

B $\Sigma - 0.450$	0.442	$\rightarrow - 0.5$
D $\Sigma - 0.470$	0.831	Co. Flocculation
F $\Sigma - 0.515$	0.445	

The anomaly in D suggests a surfactant in use in D which is somewhat excessively oleophilic, favouring easy entry into the water phase. The value of  $\Delta E$  D should have been lower in both cases if the correct structure surfactant had been employed.

It is seen from the exposure plots that the concepts offered in the Lugano and to-day's papers are relevant to the development of colour acceptance and to the formulation of the colorants to be employed.



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# Paint Adhesion to Galvanised Steel Surfaces, Part 1: Effects of binder and pigments

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## Summary

The mechanism of paint adhesion deterioration on hot-dip galvanised steel during natural weathering has been studied. Variables were the paint binder, the pigment system and the source of the galvanised steel, making 72 painted panels. The binder, the anticorrosive pigment and the surface composition of the zinc all had a pronounced effect on the performance of the system through an effect on the rate of interfacial zinc corrosion, as could be concluded from analysis of the metal paint interface after weathering. Chemical degradation of the paint itself was a negligible factor in the adhesion loss mechanism.

Statistical evaluation indicated that there are fairly strong interactions between the pigments and the binders. Some pigments did not perform well in combination with a certain binder or on a specific zinc substrate. Averaged for all zinc substrates, polyester paints pigmented with calcium borosilicate or with chromates performed best. Epoxies pigmented with zinc chromate also performed excellently, whereas epoxies containing zinc phosphate or calcium borosilicate were very poor.

The major factor in the zinc surface was found to be the presence and distribution of  $Al_2O_3$  in the oxide film. Irregular  $Al_2O_3$  distributions speed up zinc corrosion markedly by an electrochemical mechanism. The presence of  $ZnAl_2O_4$  at the zinc surface improves paint adhesion stability considerably.

## 1. Introduction

Although galvanised steel is by no means a new substrate for paint coatings, e.g. in structural steel applications<sup>1-5</sup>, the advent of new materials for the control of automotive steel corrosion, such as galvanised and electro-galvanised steel sheet, has increased the interest in the paintability of zinc considerably.

The metallurgy of batch galvanised structural steel has been studied in much detail<sup>6-9</sup>, as has the performance of many paint systems on this substrate in natural or accelerated weathering<sup>10-15</sup>. A recent review of paint systems and their performance was given by Van Eijnsbergen<sup>16</sup>, which also demonstrates that, although some progress has been made due to the application of modern surface-sensitive analytical tools<sup>17-19</sup>, the effects of the outermost zinc surface structure on adhesion to paints are not well understood. The variability in the performance of a paint system on zinc substrates from different suppliers is a well-known problem<sup>20</sup>.

Two problems encountered in the automotive industry when steel substrates were replaced with zinc substrates illustrate the need for detailed knowledge of the surface and interface chemistry of these metals. When steel is replaced with one-sided galvanised steel the phosphating treatment does not perform well on the zinc-coated side of the sheet, and secondly, problems may arise in cathodic

electrocoating of zinc instead of steel<sup>21,22</sup>. Using Auger electron spectroscopy, Kim and Leidheiser analysed the oxide film on sheet galvanised steel<sup>23,24</sup>. A large number of contaminants and a rather high Al content were found. The same authors also reported that the initial, unweathered paint adhesion was dependent on the crystallographic orientation of the zinc spangles which determined the brittleness and the deformability of the zinc layer<sup>25,26</sup>. Both transgranular and intragranular cracking of the zinc layer may occur during deformation<sup>27</sup>.

The main purpose of this study was to investigate the parameters that control the paint adhesion to zinc surfaces during natural weathering. Therefore the paint binder, the anticorrosive pigment and the source of the zinc were varied systematically. The surfaces of the zinc were characterised by surface analysis and by electrochemical methods. In the galvanised panels from one supplier one factor was varied, viz. the Al content of the zinc bath in order to study the reported effect of Al in the zinc layer in some more detail<sup>17-19</sup>.

The pigments selected were conventional chromates and some new developments which have been offered as possible chromate replacements.

In Part 1 of this study the experimental set up and the adhesion results obtained with 72 painted panels are described and discussed. In Part 2 the characterisation of the zinc surfaces and the effect of the zinc parameters on adhesion and corrosion will be reported. In Part 3 the characterisation of paint-zinc interfaces will be described and overall conclusions of this study as well as suggestions for further improvements will be given.

## 2. Methods and Materials

### 2.1 Description of experiments

Hot-rolled carbon steel panels, type 37, of 30x60 cm<sup>2</sup> dimensions and 2 mm thickness and halfway angled at 60°, were galvanised by four different Dutch galvanisers. From each galvaniser 13 panels were received, of which eight were selected on the basis of homogeneous and identical appearance. Out of these eight samples, two were selected randomly for characterisation purposes to be described in Part 2. The remaining panels were painted as soon as possible. They were divided into three sections which were brush-painted with two coats of 40µm primer on polyester, epoxy or polyurethane basis. Six formulations of each primer were used in which the anticorrosive pigment system was varied. Half of all primed surfaces were topcoated on both sides with one 40µm topcoat on polyurethane basis without anticorrosive pigment.

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A painted panel is shown schematically in Figure 1. The total number of panels in this set up was 24, namely 72 combinations (four zinc substrates, three binders and six pigments) with three paint systems applied on each panel.

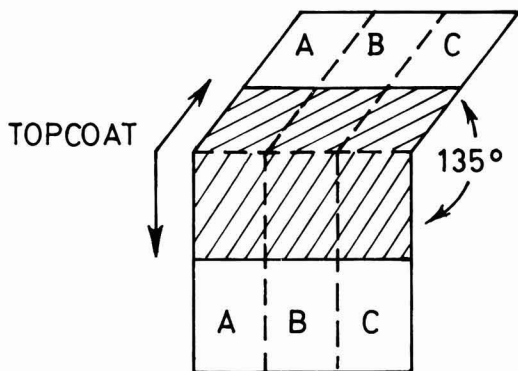


Figure 1 Test panels for paint adhesion experiments

## 2.2 Description of zinc panels

The following is a description of the types of zinc panels used:

Type I: from electrolytic zinc; rough surface; no clear spangles; some very glossy islands; inclusions of hard zinc; average thickness 63 $\mu$ m (Förster).

Type II: GOB zinc with some Sn; very smooth and homogeneous surface; large spangles; dull appearance; average thickness 80 $\mu$ m.

Type III: electrolytic zinc; no clear spangles; not homogeneous; combination of islands, spangles, stripes; average thickness 55 $\mu$ m.

Type IV: electrolytic zinc; no clear spangles; very glossy; very homogeneous; average thickness 43 $\mu$ m.

Type V: electrolytic zinc; moderate spangles; glossy; average thickness 62 $\mu$ m; this substrate was only used as a reference in the experiments with series VI-XV.

Types VI-XV: from the same galvaniser as type IV; panels were galvanised at regular intervals. During this period no Al was added to the zinc bath. The Al content decreased regularly and the appearance changed from glossy and no spangles to very dull with large spangles as shown in Table 1. The thickness increased somewhat with decreasing Al content.

## 2.3 Paint systems on zinc types I-IV

All paints were commercial or development products of Sikkens Paint Company at Wapenveld, The Netherlands.

**Binders:** Primer A was based on Dynapol L205, a saturated polyester one-component, physically drying paint; B was a Resikote binder consisting of a hydroxyacrylate crosslinked with an isocyanate; C was an amine-cured epoxy adduct. The topcoat was a Resikote

isocyanate-crosslinked hydroxyacrylate polyurethane, similar but not identical to B.

**Pigment systems:** the paint systems usually contained TiO<sub>2</sub> and talcum as fillers and extenders, series B also contained small amounts of red iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and micaceous iron oxide (Fe<sub>2</sub>O<sub>3</sub>). In addition the following anticorrosive pigments were used in combination with binders A, B and C.

**Pigment a:** standard anticorrosive pigments for these paints, viz.:

- A: zinc phosphate (37.1 vol-%); paint Aa
- B: zinc chromate (40.0 vol-%); paint Ba
- C: none; paint Ca.

**Pigment b:** Lipicor LCW 221 (calcium borosilicate from Lindgens); PVC was identical to that used in the three standard paints Aa, Ba and Ca with 40.4 vol-% for paint Cb (paints Ab, Bb, Cb);

**Pigment c:** Lipicor LCW 221 at 10 per cent below its CPVC (paints Ac, Bc, Cc);

**Pigment d:** zinc phosphate, Zn(PO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, at 10 per cent below its CPVC (from ISC Ltd); paints Ad, Bd, Cd;

**Pigment e:** zinc chromate (ZnCrO<sub>4</sub>, type 6098 from Vossen, Venlo, Neth.) at 10 per cent below its CPVC (paints Ae, Be, Ce);

**Pigment f:** strontium chromate (Ciba Geigy, type SC-08) at 10 per cent below its CPVC (paints Af, Bf, Cf).

## 2.4 Paint systems on zinc types V-XV

Three binders were used in this experiment. They were pigmented with their standard system which was not varied.

**Primer D:** polyester, identical to system A; pigmented with zinc phosphate at 37.3 vol-%;

**Primer E:** Macrynal SM 500, a hydroxyacrylate crosslinked with Desmodur N (isocyanate); similar but not identical to primer B; pigmented with Lipicor LCW at 40.0 vol-%;

**Primer F:** a physically drying phenoxy-phenol resin pigmented with zinc phosphate at 40.3 vol-%.

The test panels were identical to those of Figure 1. All primers were applied in two 40 $\mu$ m coats. Half of the panels were topcoated with one 40 $\mu$ m coat of the same polyurethane topcoat as described in Section 2.3.

## 2.5 Weathering of painted panels

The painted panels of type I-IV were exposed outdoors in an industrial environment at 20 km from the North Sea with winds prevailing from the sea. One half of the panel was kept horizontal, the other half was sloping down (see Figure 1) in southern direction. The panels were inspected and tested for adhesion every six months and on both sides. Unpainted panels of zinc types I-IV were exposed simultaneously.

The painted panels of types V-XV were exposed at the same site and for the same period. Adhesion was tested on the front side of the panels only.

## 2.6 Adhesion testing

Paint adhesion was determined by the cross-hatch method following DIN 53151 specifications which prescribe 2 mm squares and a 1-5 rating scale from good to poor. Adhesion was rated once per six months on each section indicated in Figure 1, i.e. 24 per panel.

Table 1  
Zinc panels VI-XV

No.	Per cent Al in bath	Thickness, $\mu\text{m}$		Appearance
		top front/back	bottom front/back	
VI	0.014	45/48	42/51	glossy; small spangles
VII	0.013	45/45	43/54	very glossy; large spangles
VIII	0.013	44/44	43/51	
IX	0.007	47/47	44/55	
X	0.006	44/50	46/55	
XI	0.004	48/45	44/56	
XII	0.002	46/45	55/54	
XIII	0.003	51/48	51/61	
XIV	0.001	56/61	58/66	very dull; large spangles
XV	0.001	59/59	59/68	very dull; very large spangles

Table 2  
Overall adhesion data\*

zinc	I						II						III						IV					
	topcoat						topcoat						topcoat						topcoat					
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
<b>pigment</b>																								
a	20	12	15	20	20	16	14	14	16	14	18	19	20	10	13	18	19	11	20	7	12	20	20	12
b	8	8	16	6	17	10	4	11	15	6	10	12	6	8	18	5	15	15	9	12	16	7	20	14
c	7	13	20	8	19	19	4	13	20	4	8	20	6	14	17	6	13	16	8	15	20	8	16	19
d	20	8	20	19	18	19	4	8	20	4	9	18	20	9	18	14	12	17	19	6	16	17	17	16
e	4	7	6	6	18	8	4	8	4	4	11	4	9	8	8	11	19	10	4	8	4	9	19	8
f	6	5	9	6	19	9	4	8	20	4	10	13	14	8	13	13	17	15	5	8	10	7	18	10

\*sum of the ratings top/bottom and back/front

## 2.7 Corrosion rating

In the cross-hatch adhesion measurements the amount of visible white zinc corrosion products was also rated on a 1-5 scale from low to high. Actual analysis of these products will be reported in Part 2.

## 2.8 Infrared analysis of weathered paint surfaces

In order to estimate qualitatively whether paint adhesion loss could be related to degradation of the primer during weathering, the surfaces of some weathered primers were studied by IR-ATR techniques using a 45° KRS-5 Thallium Iodide crystal. The surface area probed was  $4 \times 1\frac{1}{2} \text{ cm}^2$ .

## 2.9 Experiments with clear unpigmented polymer films

In order to estimate the corrosion protection of zinc by the polymer alone, clear, unpigmented polymer films of A, B and C were applied by spraying onto panels I-IV. On half of

the panels a wash primer was applied first. Thickness of the films was 40-60  $\mu\text{m}$ . These coated panels were exposed for 1,000 hours in a Weather-o-meter at 60°C. The degree of zinc corrosion was estimated on a qualitative basis through the coating.

## 2.10 Zinc corrosion in pigment slurries and extracts

### Slurries:

Aqueous slurries consisting of barium sulphate, anti-corrosive pigment and demineralised water (47.5, 5.0 and 47.5 vol-%, respectively) were prepared into which weighed  $2.5 \times 2.5 \text{ cm}^2$  galvanised steel samples were immersed vertically. After two weeks the samples were rinsed, lightly brushed, weighed and visually inspected.

### Extracts:

Demineralised water (50 ml) and 5g anticorrosive pigment were mixed and shaken for five days. The liquid was filtered and diluted to 250 ml. In a 50 ml extract a weighed

2.5 × 2.5 cm<sup>2</sup> galvanised steel sample was immersed vertically. After seven days the samples were rinsed, lightly brushed, weighed and inspected. Before and following immersion the pH of the extract was measured. In both tests the weight loss and the appearance of the zinc were taken as a combined measure of the anticorrosive properties of the pigments.

### 3. Results

#### 3.1 Adhesion data

Adhesion results are given for panels which had been exposed for three years. In all systems the trends observed after shorter periods of weathering were identical although less pronounced.

In the comparison of trends and effects it is assumed that each rating on the 1-5 scale has an uncertainty of ± 1. Hence the standard deviation is  $\sqrt{n}$  for each series of  $n$  data summed and  $\sqrt{2} \times \sqrt{n}$  for 2 series of  $n$  each. Significance is then observed if an effect exceeds twice the standard deviation, i.e.  $2\sqrt{2} \times \sqrt{n}$ .

In order to study first order interactions between the effects of binders, pigments and zinc surfaces, a variance analysis was carried out. For this purpose the 1-5 scale was transformed to a scale which ranges from -2.19 (good) to +2.19 (poor) using the equation:

$$R = \ln((\text{rating} - 0.5)/(5.5 - \text{rating}))$$

This transformation expands the two ends of the rating scale and results in a constant standard deviation.

#### Adhesion to panels I-IV

The overall results are given in Table 2. The figures are the sums of four ratings on the 1-5 scale taken for each panel on the horizontal and angled sections of back and front. In some of the other tables a distinction between the various locations of the panels will be made.

All unpainted panels exposed simultaneously had an uncorroded appearance. In the next series of tables some of the data of Table 2 has been summed in order to show the effects of the three major variables as well as their first order interactions.

In Table 3 the adhesion results of the four zinc surfaces summed over all pigments, binders and reference points on the panels, are given. It is observed that zinc of type II is significantly better than the others and that this is due to a markedly better performance under primer A (polyester). Under the other primers its performance is not significantly different from the other zinc types.

The factors in the zinc surface of type II that might be the underlying cause of this difference are discussed in Part 2.

In Table 4 a comparison is made of the six pigment systems. The results for the three binders are shown individually. It can be concluded that pigment e (zinc chromate) has the best overall performance, followed by strontium chromate and calcium borosilicate. The table also indicates that the performance of a certain pigment system depends on the binder in which it is used. Calcium borosilicate performs similarly to the chromates in the polyester binder but not in an epoxy, whereas in the polyurethane all pigments are about equal. Interactions

Table 3

Adhesion of four zinc types\*

Zinc	A		B		C	=	Sum
I	130	+	164	+	167	=	461
II	72	+	128	+	181	=	381
III	142	+	152	+	171	=	465
IV	133	+	166	+	158	=	457
<hr/>							
	477	+	610	+	677	=	1764

\*n=48

Table 4

Comparison of pigment systems\*

Pigment	A		B		C	=	Sum
a	146	+	120	+	115	=	381
b	51	+	101	+	116	=	268
c	51	+	111	+	151	=	313
d	119	+	87	+	144	=	350
e	51	+	98	+	52	=	201
f	59	+	93	+	99	=	251
<hr/>							
	477	+	610	+	677	=	1764

\*n=32

between the three major factors of this study are shown later in this section.

Table 4 further indicates that binder A (polyester) comes out significantly better than the other two, although from Table III it can be concluded that this difference is over-emphasised because of the very good performance of zinc type II. However, even if the results for the other three zinc types are summed, binder A is still significantly better than B and C, viz. A = 405, B = 482, C = 496 (n = 144).

If the data of Table 2 are summed in such a way as to show the effect of the polyurethane topcoat, the ratings of Table 5 are obtained. They are integrated over all pigments and for both sides of the panels, but still show the effect of the three binders. For binders A and C no significant effect of the topcoat can be seen, but for the polyurethane (B) the PU topcoat clearly has a negative effect on the performance of the system, with the exception, however, for zinc type II, which is the best of the four substrates (Table 3). One could also conclude that the polyurethane primer is rather insensitive to the pigment system used, with or without topcoat, but becomes very zinc-sensitive if it is topcoated with a PU coat.

Table 6 shows a comparison of the effects of the exposure

Table 5

Effect of topcoat on adhesion\*

Zinc	A	B	C	Sum
I	65/65	+ 53/111	+ 86/81	= 204/257
II	34/38	+ 62/66	+ 95/86	= 191/190
III	75/67	+ 57/95	+ 87/84	= 219/246
IV	65/68	+ 56/110	+ 78/80	= 199/258
<hr/>				
239/238 + 228/382 + 346/337 = 813/951				

\*n=24; xx/xx = without/with topcoat

conditions, i.e. of the back and front of the panels. The table includes the individual effects for the presence of the topcoat, the pigments, binders and zinc types. Considering the number of measurements in all cases, it can be concluded that the only significant difference is observed between back and front for the systems with pigments a and d (standard and zinc phosphate, respectively). A deterioration at the back of the panels is also observed for all primers summed without topcoat (Table 6(A)), so the topcoat has a protective effect in this respect. No effects between back and front are seen if only zinc types or individual binders are considered.

It is interesting to conclude (Tables 5 and 6) that the topcoat generally shows a negative effect on the paint adhesion, but its presence has a positive effect on the accelerated adhesion loss at the back side of the panel. The results of the analysis of variance of the adhesion data of Table 2 are presented in Table 7 and in figures 2, 3 and 4. Such an analysis shows whether there are specific interactions between the major variables. Only first order interactions are considered. Table VII shows that such interactions are indeed observed (F factor) and that some of them are significant ( $P < 0.1$ ). The degree of such interactions can best be demonstrated by plotting the transformed ratings for the three major combinations of the variables, i.e. zinc type, binder and pigment, as has been done in Figures 2-4. Figure 2 shows that there are specific combinations of pigments and binders that are better than others, regardless of the type of zinc. Although this graph emphasises the dependence of adhesion on a specific combination pigment-binder, the conclusions are identical to, and confirm those of Table 4; the best systems are chromates with polyester, zinc chromate with epoxy or calcium borosilicate with polyester. Calcium borosilicate or zinc phosphate with epoxy is particularly poor.

In figures 3 and 4 interactions between zinc types and either binder or pigment are shown. The magnitude of these interactions is clearly much smaller than those of Figure 2, but they are nonetheless significant. The best zinc-pigment combination is II with e (zinc chromate), the poorest is either I with d (zinc phosphate) or I with a. Calcium borosilicate appears to be the second best pigment.

The best zinc-binder combination (Figure 3) is clearly II-polyester, whereas the same zinc with an epoxy binder is

Table 6

Comparison of front and back of panels

A. Effect of topcoat*				
	Front		Back	Sum
no topcoat	381	+	432	= 813
with topcoat	484	+	467	= 951
<hr/>				
	865	+	899	= 1764

\*n=144

B. Effect of binder*				
Binder	Front		Back	Sum
A	238	+	239	= 477
B	297	+	313	= 610
C	330	+	347	= 677
<hr/>				
	865	+	899	= 1764

\*n=96

C. Effect of pigment system*				
Pigment	Front		Back	Sum
a	175	+	206	= 381
b	142	+	126	= 268
c	149	+	164	= 313
d	165	+	185	= 350
e	104	+	97	= 201
f	130	+	121	= 251
<hr/>				
	865	+	899	= 1764

\*n=48

D. Effect of zinc substrate*				
Zinc	Front		Back	Sum
I	226	+	235	= 461
II	189	+	192	= 381
III	232	+	233	= 465
IV	218	+	239	= 457
<hr/>				
	865	+	899	= 1764

\*n=72

the poorest. These conclusions are in agreement with those of Table 3.

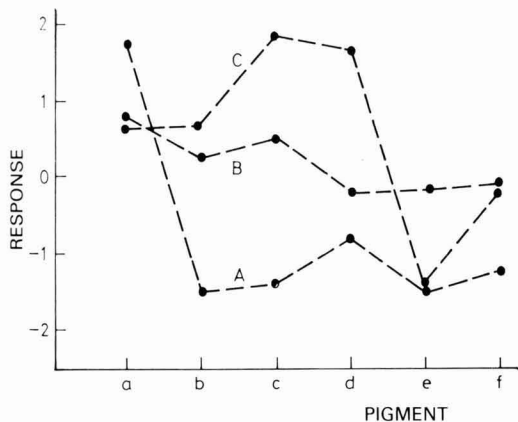


Figure 2 Transformed paint adhesion ratings showing first order interactions between binders and pigment systems

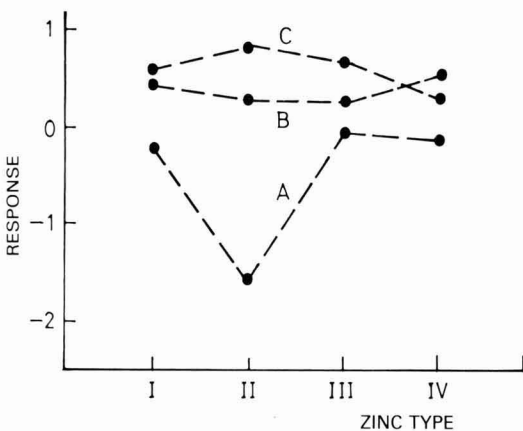


Figure 3 Transformed paint adhesion ratings showing first order interactions between binders and type of zinc substrate

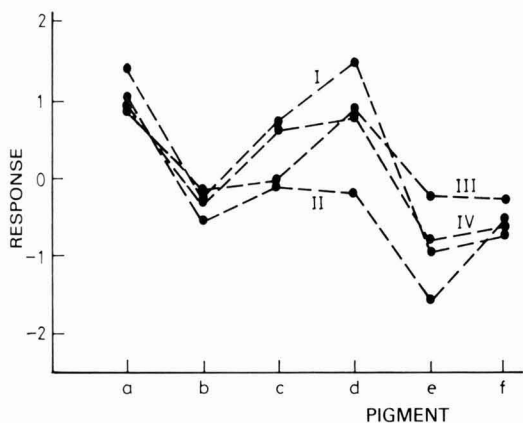


Figure 4 Transformed paint adhesion ratings showing first order interactions between type of zinc substrate and pigment systems

### Adhesion to panels V-XV

All results of this experiment, in which primarily the effect of varying the Al content of the zinc bath was investigated, are presented in Table 8. Further variables were the binder of the primer and the presence of a topcoat. Adhesion was only evaluated at the front side of the panels at both the horizontal and the angled sections. The following conclusions can be drawn from the data:

1. There is a tendency that the panels prepared from zinc with low Al content perform more poorly for the three points, although the performance of D is poor on all substrates;
2. Paint F reacts more sharply to low Al contents, especially when topcoated;
3. For paints D and E performance also drops somewhat if they are topcoated;
4. Zinc V behaves very similarly to zinc IV. The latter performs under paint D as poorly as under paint A, whose formulations were very similar. Since zinc types V-XV were supplied by the same galvaniser as type IV, it must be concluded that variations of the Al content in the bath do not affect performance markedly, at least for the systems investigated here;
5. There is a dramatic difference between the paints D and F, except for the topcoated panels with very low Al content XIV and XV, although these paints contain the same pigment system. This implies that the binder is the more important factor in paints for galvanised steel.

### 3.2 Performance of clear unpigmented paint films

Corrosion of zinc under clear paint films should be considered with due regard to the limitations of the experiment. Factors such as porosity and water diffusion, UV stability, etc., which are all strongly affected by the pigment system, have completely been ignored. Indeed, after 1,000 hours of Weather-o-meter ageing, it was observed that all zinc panels coated with clear binder films of A and C (polyester and epoxy) were severely corroded. Corrosion under the polyurethane binder was considerably less. Whilst this experiment indicates differences between corrosivity of the pure binder films on the one hand, it also confirms that only combinations of binders with pigments should be considered, as was conclusively shown in Figure 2.

### 3.3 Zinc corrosion in pigment slurries and extracts

Here, too, results should be considered with some reservation since specific pigment-binder interactions, such as adhesion, are ignored. Further, the concentrations of the corrosion-inhibiting species in these experiments and in actual paints may be entirely different.

The results are summarised in Table 9. It is seen that in both tests all pigments used in this study are effective corrosion inhibitors of galvanised steel. There is a good correlation between the results in the two tests. Corrosion inhibition results in a much reduced weight loss and in the prevention of corrosion spots at the zinc surfaces. It is also observed that calcium borosilicate maintains a rather pH in the solution, and finally that different versions or brands of



the same pigment, e.g. zinc phosphate, can show greatly different performances.

Although results of such model experiments cannot be entirely conclusive, it seems that a candidate pigment should at least show a good qualitative performance in such tests. Pigments which fail in this test do not perform well in

paints. This has been confirmed for a wide range of paint systems on zinc substrates.

### 3.4 Infrared studies of weathered paint surfaces

Two sets of samples were investigated:

- a: paints Aa, Ba, Ca on a zinc substrate, weathered outdoors for 12 months;
- b: the clear, unpigmented paint films described under 3.2 but now on an Al substrate; weathered for 1,000 hours in a Weather-o-meter.

All samples were also studied before weathering. Some depth information could be obtained by using two different thallium iodide crystals with different angles of incidence.

The results can be summarised as follows:

In all weathered formulated paint films the intensity of the absorption frequencies of the polymer decreases markedly. The absorption spectrum of the pigment (zinc phosphate) becomes dominant. This effect is most pronounced for the epoxy binder. In none of the three binders hydrolysis of the polymer can be detected, i.e. no carboxyl or carboxylate groups are observed.

In the unpigmented polymer films aged in the Weather-o-meter a strong hydrolysis has occurred, as evidenced by the presence of carboxyl and carboxylate groups. In the epoxy film carbonyl groups are also formed during weathering. Comparison of the results obtained with the two crystals shows that the concentrations of these newly formed groups decrease with depth for all three polymers.

These combined results indicate that the reactions in unpigmented films in a Weather-o-meter are probably entirely different from those which occur in the actual paint films during natural weathering. Hence, the performance of the unpigmented films on zinc cannot be related to actual paint performance (Section 3.2). In the paints the binder is

Table 7

First order interactions between variables\*

Interaction	F†	P
PB	28.73	<0.001
ZB	10.18	<0.001
PZ	4.14	<0.001
PS	3.86	0.003
ZS	<1	
BS	<1	
TS	8.76	0.004
PT	4.65	<0.001
ZT	5.92	<0.001
BT	45.49	<0.001
PU	2.31	0.05
ZU	2.01	
SU	6.15	0.01
BU	<1	
TU	1.57	

\*P, pigment; B, binder; Z, zinc; S, side; T, topcoat; U, top/bottom.

†Interaction parameter

Table 8

Paint adhesion to panels IV-XV\*

Panel	front, horizontal						front, 45° angle					
	primer			topcoat			primer			topcoat		
	D	E	F	D	E	F	D	E	F	D	E	F
IV	5	0	0	5	1	0	5	0	0	5	1	0
V	4	1	0	5	2	0	5	2	0	5	2	0
VI	4	1	0	5	1	0	5	0	0	5	1	0
VII	4	1	0	5	0	0	5	2	0	5	4	0
VIII	4	2	0	5	1	0	5	1	0	5	1	0
IX	5	0	0	5	1	0	5	0	0	5	2	0
X	1	1	0	2	1	0	5	4	0	5	1	0
XI	5	2	0	5	2	0	5	2	0	5	2	0
XII	5	3	0	5	3	0	5	2	0	5	3	0
XIII	5	1	0	5	2	0	5	2	0	5	2	1
XIV	5	1	1	5	3	4	5	3	2	5	5	5
XV	5	0	0	5	3	3	5	5	5	5	5	5

n=1; three years exposure

slowly eroded and washed out but no hydrolysis has taken place in the part of the film that remains. Although the epoxy seems to erode more rapidly, this does not seem to result in a poorer performance of the zinc phosphate-pigmented paint (see Figure 2).

#### 4. Discussion

The data presented in the previous section lead to the conclusion that paint adhesion during natural weathering of painted galvanised steel is a very complex phenomenon since it is determined by three major factors. These are the paint binder, the anticorrosive pigment system used and the quality of the zinc substrate. These factors are not independent but show strong interactions. Therefore, in order to obtain the best possible performance on galvanised steel, a paint system should be optimised for that type of zinc.

It is not the purpose of this paper in the series to provide mechanisms for the effects observed. This will be done in parts 2 and 3. However, some important conclusions can already be drawn in this paper.

The adhesion data combined with the IR studies of the paint films suggest strongly that, at least during natural weathering, degradation of the paint binder does not play a major role in the adhesion loss mechanism. This follows, for instance, from Table 4 where paint adhesion is not significantly different for the side that has been exposed to the sun or the side that has contained more moisture during the test period. This conclusion applies to the three binders used.

It can, on the other hand, be demonstrated that there is a relationship between the degree of interfacial zinc corrosion and the experimentally observed adhesion. This is shown in Table 10 which lists adhesion ratings for the 18 paint systems summed over the four zinc types after one year of natural weathering. Data are given for the three binders individually and summed over A, B and C. In the same table the corrosion ratings on a 1-5 scale are shown of the same systems. All data are averaged by dividing the

Table 9  
Corrosion in pigment extracts\*

Pigment	Weight loss†	pH	Percentage corroded
Strontium chromate	0.8	7.68	0
Zinc chromate	0.9	7.75	0
Zinc phosphate	1.0	7.26	40
Calcium borosilicate	1.7	9.58	0
Zinc borate	2.8	7.58	40
Zinc phytate	4.6	7.63	60
Demineralsed water	6.9	8.12	90

\*Zinc of type IV  
†In mg/3g

Table 10  
Adhesion vs. interfacial corrosion\*

Binder A			Binder B		
pigment	adhesion	corrosion	pigment	adhesion	corrosion
f	1.19	1.16	f	2.22	1.66
b	1.19	1.16	d	2.28	1.59
e	1.41	1.16	e	2.44	1.63
c	1.62	1.13	b	2.53	1.72
d	1.41	1.47	c	2.69	1.42
a	3.28	1.84	a	3.09	2.22

Binder C			Total		
pigment	adhesion	corrosion	pigment	adhesion	corrosion
e	1.41	1.03	e	1.75	1.27
f	2.50	1.47	f	1.97	1.42
a	2.50	2.00	b	2.22	1.70
d	2.75	2.34	d	2.47	1.80
b	2.94	2.22	c	2.76	1.97
c	3.97	3.34	a	2.96	2.02

\*n=32

total rating by the number of measurements (32 or 96). It is seen that the ranking of the pigments is the same as that observed after three years of weathering. Remarkable is the poor performance of pigment c in the epoxy primer after this rather short period of ageing. More importantly, however, it can be concluded that the loss of adhesion parallels the corrosion rating. This correlation is relatively weak for the polyurethane binder which is not very sensitive to the pigment system (cf. Figure 2) but is very strong for the two other primer binders and for the sum of the three. It can thus be concluded that paint adhesion to galvanised steel is determined by the rate at which corrosion reactions can proceed at the interface zinc-paint. This corrosion rate is determined by the quality of the substrate, the pigment system, the paint binder and also by the combination of the pigment and the binder. The mechanisms of these effects will be discussed further in parts 2 and 3. Here, a general model is presented for the strong interactions between pigments and binders as is shown in Figure 2.

Figure 2 indicates that there are three levels of corrosion protection which can be distinguished, *viz.*:

1. Systems with responses between +1 and +2; polyester with pigment a, epoxy with c or d;
2. systems with intermediate responses, between +1 and -0.5; all polyurethane paints, epoxy with a, b and f;
3. systems with good corrosion protection, with responses between -0.5 and -2.0; polyester with b-f and epoxy with e.

In view of the observed relationship between adhesion and interfacial corrosion (Table 10) it must be inferred that the rate of zinc corrosion is highest in group a and lowest in group c. In group b, all of the polyurethane-based paints show approximately the same rate of corrosion. This must, in view of the differences between inherent corrosion inhibition efficiency of the various pigments (cf. Table 9) mean that in the polyurethane paint the pigment is almost ineffective. It is known that polyurethane groups provide a very high level of initial, uncorroded adhesion to many substrates, e.g. in adhesives. Therefore it is assumed that the corrosion inhibition of the polyurethane-based paints is totally due to the strong initial adhesion to the zinc substrates. The absence of pigment effects, in this model, is the result of an equally strong adhesion of the polymer to the pigment particles. In agreement with this, it has been found that extraction of polyurethane paints yields much less soluble material (pigments) than, for instance, epoxy paints<sup>28</sup>. In the polyester paints (group c) the adhesion to the substrates and to the pigment particles is lower than in the polyurethanes. Hence the pigment particles are extractable during weathering and will perform as corrosion inhibitors. Calcium borosilicate and zinc phosphate both perform as such by maintaining a rather high and constant pH at the paint-metal interface, as will be demonstrated in Part 3 of this series<sup>29</sup>. As a result, such inhibitors will not perform well if, for any reason, the pH at the interface drops to acidic values. The reason why system Aa, which also contains zinc phosphate, performs very poorly, is unknown. The PVC of the pigment, as compared to system Ad, was different which may have an effect on the extractability of the pigment.

The chromates inhibit corrosion by an entirely different

mechanism, as will also be shown in Part 3 in more detail. They form an in situ passive film on the metal surface and hence, they are effective anodic inhibitors. This mechanism is almost independent of the pH. Therefore they are more universally applicable. In the epoxy series, for instance systems Cc and Cd, the poor performance is most likely the result of a rather low pH at the metal surface, as has been described<sup>16</sup>, especially during weathering in industrial environments. Under these conditions the pH-regulating buffering pigments c and d have no anticorrosive properties at all. In fact, as compared to system Ca, which has no anticorrosive pigment at all, high concentrations of c and d now increase the rate of corrosion. Polyester polymers do not develop an acidic pH during weathering and as a result, pigments b, c and d now perform much better. The difference between the epoxy and polyurethane polymer in this respect may be related to different rates of hydrolysis of the polymer at the interface or to differences between the uptake of SO<sub>2</sub> during weathering. Analysis of the products formed at the interfaces may resolve this aspect further (see Part 3).

In conclusion, this rather simple model for pigment-polymer interactions predicts that paint performance on galvanised steel is determined by the level of initial adhesion of the polymer to the metal and to the pigment particles, the efficiency of the corrosion-inhibiting pigment, which should be extractable to some extent, and by the hydrolytic stability of the polymer vehicle. It should be noted that all of these parameters can, in principle, be determined for a given system, without actually performing weathering experiments.

## 5. Conclusions

The conclusions of this part of the study of paint adhesion retention during natural weathering of painted galvanised steel are as follows:

- Adhesion retention is related to the rate of zinc corrosion at the interface.
- There are three major factors which determine the rate of zinc corrosion, *viz.* the type of binder, the anticorrosive pigment system and the quality of the zinc surface.
- There are first order interactions between these factors which are particularly strong between pigment and binder. This implies that only specific combinations of pigment and binder perform well on a certain zinc substrate. It also implies that certain pigments perform well in certain binders but not in others.
- Chromate pigments perform well in the three binders investigated (polyester, epoxy and polyurethane).
- Calcium borosilicate pigment may replace chromates for applications on galvanised steel but only in combination with a polyester binder.
- The choice of the binder system appears to have the greatest effect on the performance of the entire system;
- Degradation of the polymer vehicle during weathering does not contribute significantly to the degradation of paint adhesion.
- The presence of a PU topcoat without anticorrosive pigment does not improve paint adhesion, except on zinc of very good quality. Although the level of adhesion is reduced by the topcoat, the rate of further degradation of adhesion is retarded.
- Galvanised steel shows poorer performance if the amount of aluminium in the zinc bath is reduced

strongly. Above a certain level, however, the Al content is not critical.

- A model has been presented which explains the strong pigment binder interactions on the basis of adhesion of the polymer to the pigment particles, the hydrolytic stability of the polymer vehicle at the interface and the mechanism of the corrosion inhibition by the pigment. Important as to whether this inhibition is pH-dependent or not.

## 6. Acknowledgements

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## 7. References

1. Kruse, C. L., *Werkst. u. Korr.*, 1976, **27**, 841.
2. Burgmann G. and Meyer K., *Bänder, Bleche, Röhre*, 1979, **2**, 78.
3. Takahashi H., Shirogane Y., Matsudo K., Adaniya T. and Omura M., *SAE Tech. Paper Ser.*, 800145, 1980.
4. Haagen, H., *Ind. Lackierbetr.*, 1982, **50**, 221.
5. Van Oeteren, K. A., *Werkst. Korr.*, 1982, **33**, 467.
6. Bastin, G. F. and Van Loo, F. J. J., *Z. Metallk.*, 1978, **69**, 540.
7. Mackowiak, J. and Short, N. R., *Int. Met. Revs.*, 1979, **24**, 1.
8. Pelerin, J., Hoffmann, J. and Leory, V., *Metall.*, 1981, **35**, 1.
9. Fellner, P., Lubyova, Z. and Pohl, D., *Chem. Zvesti*, 1982, **36**, 327.
10. Dalton, D. L., *Paint Manuf.*, 1977, **47**, 21.
11. Van Oeteren, K. A., *Metall.*, 1978, **32**, 906.
12. Clothier, A. D., *JOCCA*, 1981, **64**, 294.
13. Bieganska, B. and Smieszka, E., *Prog. Org. Coat.*, 1982, **10**, 215.
14. Brasholz, A., *Mappe*, 1982, **102**, 163.
15. Glasscock, R. M., "Corrosion 83", NACE, 1983, paper no. 34.
16. Van Eijnsbergen, J. F. H., Fourth Conference on Recent Developments in the Field of Corrosion Science and Engineering; Johannesburg, South Africa, August 6-8, 1985.
17. Van Ooij, W. J., *Proc. UK Nat. Corr. Conf.*, 1982, 7.
18. Van Ooij, W. J., Leijenaar, S. R. and Van den Bergh, B., *Proc 16th FATIPEC Congress*, Liege, Belgium, May 1982, Vol. 2, 271.
19. Van Ooij, W. J., in: Parfitt, G. D. and Patsis, A. V., Eds., "Organic Coatings Science and Technology", Vol. 6, *Marcel Dekker, New York*, 1984, 277.
20. Wakano, S., Sakoda, A., Hishihara, M. and Terasaki, F., *Surfaces (Fr.)*, 1983, **22**, 65.
21. Froman, G. W. and Franks, L. L., *Proc. Conf. on Technol. Impact of Surf.*, Dearborn, Mich., USA, April 14-15 1981, 315.
22. Rausch, W., *Ind. Lackierbetr.*, 1981, **49**, 413.
23. Leidheiser, H. and Kim, D. K., *Mod. Paint Coat.*, 1976, 1.
24. Kim, D. K. and Leidheiser, H., *Surf. Technol.*, 1977, **5**, 379.
25. Leidheiser, H. and Kim, D. K., *J. Met.*, 1976, **28**, 19.
26. Leidheiser, H. and Kim, D. K., Sec. Ann ILZRO Galv. Seminar, St. Louis, Mo., USA, June 9-10, 1976.
27. Cameron, D. I. and Harvey, G. J., 8th Int. Conf. on Hot Dip Galv., London, 1967.
28. Unpublished work performed at Sikkens Research Laboratories, Wapenveld, The Netherlands.
29. Unpublished work on the performance of corrosion-inhibiting pigments.

# Non-phthalic alkyd resins based on maleopimaric acid

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## Abstract

Long, medium and short oil alkyds were prepared from rosin-maleic adduct, maleopimaric acid and phthalic anhydride separately using monomeric dehydrated castor oil. The film properties of non-phthalic alkyds were compared with those of conventional phthalic alkyds. It was observed that the films of maleopimaric acid based non-phthalic alkyds (long, medium and short oil) were better in scratch hardness, rocker hardness, alkali and solvent resistance than the conventional phthalic anhydride based alkyd films, the other film characteristics, however, were

comparable. The maleopimaric acid based alkyd films gave better performance than the films of rosin maleic adduct based alkyd.

## Introduction

Alkyd resins are the reaction products of poly-basic acid, polyhydric alcohol and monobasic fatty acid or oil. These resins today comprise about half of all the resins used in surface coating industry. In spite of a large number of other synthetic resins being available for use in paint formu-

lations, the alkyd resins surpass all of them in versatility, and low cost; combining a broad spectrum of performance properties with economy. The cost of the alkyd resins can be further reduced by substituting phthalic anhydride partially or wholly with rosin based polybasic acids such as rosin-maleic adduct, maleopimaric acid, and fumaropimaric acid. Rosin, as it is, suffers from certain inherent drawbacks such as low softening point, brittle nature, poor water resistance and high susceptibility to atmospheric oxidation, but these defects of rosin can be overcome to some extent through reactions like maleinisation in which the conjugated double bonds in rosin acids form adduct with maleic anhydride. The basic plus advantage in favour of rosin as raw material for non-phthalic alkyds is its abundant availability and low cost.

Technical information available on non-phthalic alkyds is scanty. Resin acids (like abietic acid, levopimaric acid, neoabietic acid and palustric acid) combine with maleic anhydride through Diels-Alder reaction which has been extensively investigated by several workers<sup>1-13</sup>. Silver<sup>14</sup> prepared fumaropimaric acid (tricarboxylic acid) from rosin-maleic adduct and obtained alkyd resins by combining with fatty acids and glycerol. The prepared alkyd resin was reported to have good exterior durability. Balkrishna *et al*<sup>15</sup> prepared Diels-Alder adducts of sunflower oil with various dienophiles, like maleic anhydride, dimethyl maleate, acrylic acid, and obtained alkyd resins from these adducts by partially replacing phthalic anhydride content. The product had improved scratch hardness, alkali resistance and shorter drying time.

The limitations of the product reported so far in the literature have been that the rosin adduct with dienic acids contains a significant quantity of unreacted compounds which adversely affect the film properties of alkyds prepared therefrom. The present paper reports a detailed study on non-phthalic alkyds prepared from rosin-maleic adduct and maleopimaric acid. The maleopimaric acid had been isolated from the rosin-maleic adduct by selective extraction with solvents followed by purification by crystallisation. The properties and the performance characteristics of these non-phthalic alkyds have been compared with those of the conventional phthalic alkyds.

## Experimental

### Materials

**Rosin:** N grade, acid value 166.0, softening point 69°C, volatile matter 1.1 per cent, matter insoluble in toluene 0.1 per cent, and ash content 0.02 per cent.

**Maleic anhydride:** Riedal, AR grade.

**Phthalic anhydride:** LR grade.

**Glycerol:** Sarabhai Merck, LR grade.

**Ethylene glycol:** Sarabhai Merck, LR grade.

**Dehydrated castor oil (DCO):** Commercial, acid value 5.1, iodine value 136.0, hydroxyl value 18.0, viscosity (25°C) 2.0 poises and colour 16.8Y + 2.1R.

**Driers:** Lead octoate (metal content 24 per cent) and cobalt naphthenate (metal content 4.5 per cent).

**Solvents:** All solvents used were of the commercial grade.

### Preparation of rosin-maleic adduct

Rosin was melted under an inert atmosphere and maleic anhydride (29 per cent by weight of rosin) was added to the

molten mass with continuous stirring. The temperature was then raised to 190°C and maintained for 2.5 hours. The adduct has a softening point of 112-113°C, acid value 380 and contained 0.6 per cent free maleic anhydride.

### Isolation of maleopimaric acid

The rosin-maleic adduct prepared as above was extracted with a solvent mixture of MTO and toluene (10:1). The extract was concentrated to about 40 per cent non-volatile matter and allowed to stand at 20°C overnight when crude maleopimaric acid crystallised out. This was purified by repeated crystallisation (three times) from the same solvent mixture. The yield of maleopimaric acid was 60 per cent on the basis of rosin. The maleopimaric acid obtained in this manner has an acid value 420, melting point 228.5°C and an optical rotation of

$$[\alpha]_{26.5^{\circ}\text{C}}^{\text{D}} = -32.1.$$

### Preparation of rosin-maleic adduct non-phthalic alkyds

DCO and glycerol were taken in a three-necked flask fitted with stirrer, condenser and thermometer. Inert gas (N<sub>2</sub>) was passed to the reaction mixture through a glass tube. The mixture was heated to 200°C and 0.1 per cent catalyst (lime and litharge in the ratio of 1:1) on the weight of oil was added. The temperature was raised to 240°C and maintained for one hour after which the temperature was lowered to 200°C. At first, ethylene glycol and thereafter rosin-maleic adduct were added slowly to the reaction mixture. The temperature was raised to 250°C again slowly and steadily and maintained till desired acid value and viscosity were obtained.

The above procedure was used for preparing long, medium and short oil alkyds using the following formulations:

Ingredients	Long oil alkyd (parts by wt)	Medium oil alkyd (parts by wt)	Short oil alkyd (parts by wt)
DCO	600	660	600
Rosin-maleic adduct	240	540	750
Glycerol	50	84	72
Ethylene glycol	25	84	144

### Preparation of maleopimaric non-phthalic alkyds

Long, medium and short oil non-phthalic alkyds using maleopimaric acid in place of rosin-maleic adduct were prepared by the same procedure and formulations as adopted above in rosin-maleic adduct based non-phthalic alkyds.

### Preparation of conventional phthalic alkyds

DCO and glycerol were heated to prepare monoglycerides in the manner described above and then DCO fatty acids (in the case of long oil alkyd) and phthalic anhydride were added to the reaction mixture at 180°C. Temperature was further raised to 240°C and maintained till the desired acid value and viscosity were obtained. The following formulations were used for the preparation of long, medium and short oil alkyds.



Ingredients	Long oil alkyd (parts by wt)	Medium oil alkyd (parts by wt)	Short oil alkyd (parts by wt)
DCO	340	315	300
DCO fatty acids	232		
Phthalic anhydride	200	224	300
Glycerol	108	119	195

### Characterisation of alkyds

Different alkyds prepared as above were characterised by determining their acid value, viscosity and colour. The characteristics of long, medium and short oil alkyds are given in tables 1, 3 and 5 respectively.

### Evaluation of film performance of alkyds

Both air-dried and baked film properties of long, medium and short oil alkyds were determined. The results of the film properties (air-dried and baked) of long, medium and short oil alkyds are given in tables 2, 4 and 6 respectively.

## Results and Discussion

### Long oil alkyds

Table 1 shows the general characteristics of long oil alkyds prepared from rosin-maleic adduct, maleopimaric acid and conventional phthalic anhydride. The acid value of the alkyds generally has been below 5 except for the maleopimaric based non-phthalic alkyd which showed a slightly higher acid value of 7.7. Viscosity (50 per cent solution in MTO) of maleopimaric based non-phthalic and conventional phthalic alkyds were equal (2.2 poises) while the

rosin-maleic adduct based non-phthalic alkyd had a lower viscosity of 1.0 poise at 25°C. The colour of the maleopimaric acid based non-phthalic alkyd was comparatively superior to both the other alkyds.

The film properties of these alkyd resins are shown in Table 2.

**Drying time:** No differences among the different types of alkyds were noted with respect to the drying time as all the long oil alkyds showed surface drying time of two hours, hard drying time of eight hours and tack-free time of 36 hours.

**Scratch hardness:** The film of the maleopimaric acid based alkyd showed a scratch hardness of air-dried/baked film as 1200/1400g, rosin-maleic adduct based alkyd 1100/1250g, and the conventional phthalic alkyd 900/1050g. The scratch

Table 1  
Characteristics of long oil alkyds

S1. No.	Product	Acid value	Viscosity at 25°C of 50 per cent solution in MTO (Poise)	Colour of 50 per cent solution in MTO (Lovibond units)
1.	Rosin-maleic adduct non-phthalic alkyd	4.3	1.0	24.6Y + 7.5R
2.	Maleopimaric non-phthalic alkyd	7.7	2.2	22.0Y + 5.5R
3.	Conventional phthalic alkyd	4.0	2.2	25.4Y + 8.7R

Table 2  
Film properties of air-dried and baked films of long oil alkyds

S1. No.	Product	Drying time in hrs			Hardness		Flexibility and adhesion ¼" mandrel	Impact 2 lbs from 24" height	Water resistance (48 hrs)	Acid resistance (2% H <sub>2</sub> SO <sub>4</sub> )		Alkali resistance (2% Na <sub>2</sub> CO <sub>3</sub> )		Solvent resistance (MTO)	
		SD	HD	TF	Scratch (g)	Rocker				24 hrs	48 hrs	4 hrs	8 hrs	24 hrs	48 hrs
<b>1. Air-dried</b>															
(i)	Rosin-maleic adduct non-phthalic alkyd	2	8	36	1100	12	P	P	3	5	5	5	0	5	4
(ii)	Maleopimaric non-phthalic alkyd	2	8	36	1200	14	P	P	4	5	5	5	1	5	4
(iii)	Conventional phthalic alkyd	2	8	36	900	10	P	P	4	5	5	5	0	5	4
<b>2. Baked</b>															
(i)	Rosin-maleic adduct non-phthalic alkyd				1250	18	P	P	4	5	5	5	0	5	5
(ii)	Maleopimaric non-phthalic alkyd				1400	20	P	P	5	5	5	5	1	5	5
(iii)	Conventional phthalic alkyd				1050	14	P	P	5	5	5	5	0	5	5

5 = Film practically unaffected  
4 = Slight loss in gloss  
3 = Slight blushing and loss of gloss

2 = Heavy blushing and complete loss of gloss  
1 = Partial film lift off  
0 = Complete film lift off

P = Pass (ie no cracking or detachment of film)  
F = Fail (ie slight cracking of film)

hardness value of the baked films were higher than that of air-dried films.

**Rocker hardness:** The rocker hardness of air-dried film of maleopimaric acid alkyd was the highest followed by rosin-maleic adduct alkyd and phthalic alkyd. Maximum rocker hardness of 20 was obtained with the baked films of maleopimaric based non-phthalic alkyd. Like scratch hardness, the rocker hardness of the baked films was also higher than that of air-dried films.

**Flexibility:** Air-dried and baked films of all the alkyds showed no visible damage to the film, such as cracking or detachment, on a 1/4 inch mandrel in the flexibility test.

**Impact resistance:** All the long oil alkyd films (air-dried and baked) passed the impact resistance test (2lbs from 24 inch height) as no cracking or detachment of any film was noticed.

Table 3  
Characteristics of medium oil alkyds

S1. No.	Product	Acid value	Viscosity at 25°C of 50 per cent solution in xylene (Poise)	Colour of 50 per cent solution in xylene (Lovibond units)
1.	Rosin-maleic adduct non-phthalic alkyd	15.2	1.0	22.2Y + 5.9R
2.	Maleopimaric non-phthalic alkyd	19.6	2.2	20.6Y + 4.8R
3.	Conventional phthalic alkyd	12.7	2.0	23.4Y + 6.6R

**Water resistance:** Water resistance of all the alkyd films improved upon baking in comparison to the air-dried films. Baked films of alkyds based on maleopimaric acid and phthalic anhydride were not affected in water after 48 hours of immersion whereas under the same conditions, the rosin-maleic adduct based alkyd films exhibited a slight loss of gloss. However, the air-dried films showed slight loss in gloss in case of the maleopimaric acid based alkyd and phthalic-alkyd but considerable loss of gloss accompanied with slight blushing was observed in case of rosin-maleic adduct based alkyd films.

**Acid resistance:** Acid resistance test after 48 hours immersion indicated superior resistance of both air-dried and baked films of all the long oil alkyds.

**Alkali resistance:** The alkali resistance of all the air-dried and baked alkyd films had been found to be poor. Although during the first four hour treatment with two per cent Na<sub>2</sub>CO<sub>3</sub> solution no effect was observed on the baked or air-dried films, after eight hours of treatment the results became more clear. The films (both baked as well as air-dried) of alkyds based on rosin-maleic adduct and phthalic anhydride were completely lifted off whereas the films of maleopimaric acid based alkyd showed only partial film lift-off.

**Solvent resistance:** The solvent resistance of the baked films was comparatively better. However, in case of air-dried films, only slight loss in gloss of the film was observed during solvent immersion and after 48 hours, gloss loss was complete.

#### Medium oil alkyds

Table 3 shows the general characteristics of the medium oil

Table 4  
Comparison of film properties of air-dried and baked films of medium oil alkyds

S1. No.	Product	Drying time in hrs			Hardness		Flexibility and adhesion 1/4" mandrel	Impact resistance from 24" height	Water resistance (48 hrs)	Acid resistance (2% H <sub>2</sub> SO <sub>4</sub> )		Alkali resistance (2% Na <sub>2</sub> CO <sub>3</sub> )		Solvent resistance (MTO)		
		SD	HD	TF	Scratch (g)	Rocker (g)				24 hrs	48 hrs	4 hrs	8 hrs	24 hrs	48 hrs	
<b>1. Air-dried</b>																
(i)	Rosin-maleic adduct non-phthalic alkyd	1.5	6	24	1250	16	P	P	3	5	4	5	0	5	4	
(ii)	Maleopimaric non-phthalic alkyd	1.5	6	24	1400	22	P	P	4	5	5	5	1	5	5	
(iii)	Conventional phthalic alkyd	1.5	6	24	1150	12	P	P	4	5	5	5	0	5	4	
<b>2. Baked</b>																
(i)	Rosin-maleic adduct non-phthalic alkyd				1400	19	P	P	4	5	5	5	0	5	5	
(ii)	Maleopimaric non-phthalic alkyd				1600	25	P	P	5	5	5	5	1	5	5	
(iii)	Conventional phthalic alkyd				1200	16	P	P	5	5	5	5	0	5	5	

5 = Film practically unaffected  
4 = Slight loss in gloss  
3 = Slight blushing and loss of gloss

2 = Heavy blushing and complete loss of gloss  
1 = Partial film lift off  
0 = Complete film lift off

P = Pass (ie no cracking or detachment of film)  
F = Fail (ie slight cracking of film)

alkyds prepared from the rosin-maleic adduct, maleopimaric acid and the conventional phthalic anhydride. On examination, the table shows that all the alkyd samples had acid value ranging between 10-20. However, the rosin-maleic adduct and maleopimaric acid based alkyds had slightly higher acid value than the conventional phthalic alkyds. The viscosities of 50 per cent solutions in xylene of all the samples were close to each other though the rosin-maleic adduct based alkyd gave the lowest viscosity. The colours of all the alkyds were also quite close to each other.

The film properties of the medium oil alkyd resins are shown in Table 4.

**Drying time:** The air-drying properties of all the three types of alkyds were the same, i.e. surface drying time one-and-a-half hours, hard drying time six hours, and tack-free time 24 hours.

Table 5  
Characteristics of short oil alkyds

Sl. No.	Product	Acid value	Viscosity at 25°C of 50 per cent solution in xylene (Poise)	Colour of 50 per cent solution in xylene (Lovibond units)
1.	Rosin-maleic adduct non-phthalic alkyd	22.4	0.7	23.2Y + 5.9R
2.	Maleopimaric non-phthalic alkyd	26.6	1.6	22.7Y + 4.8R
3.	Conventional phthalic alkyd	27.5	1.5	23.6Y + 6.6R

**Scratch hardness:** The air-dried/baked films of maleopimaric acid alkyd showed scratch hardness 1400/1600g, the rosin-maleic adduct alkyd 1250/1400g and conventional phthalic alkyd 1150/1200g. The scratch hardness of baked films was significantly higher than that of the air-dried films.

**Rocker hardness:** Air-dried film of maleopimaric alkyd showed the maximum rocker hardness at 22 while phthalic alkyd gave the minimum at 12. Similarly the baked films of maleopimaric acid alkyd showed the highest rocker hardness of 25 whereas that of phthalic alkyd the lowest at 16.

**Flexibility:** All the air-dried and baked films of the alkyds passed the flexibility test on a 1/4 inch mandrel.

**Impact resistance:** All the films (air-dried and baked) of alkyds passed the impact resistance test (2 lbs from 24 inch height).

**Water resistance:** Baked films of maleopimaric acid based alkyds and phthalic alkyds showed no on site effect after 48 hours while their air-dried films gave slight loss in gloss in the same period. The baked film of rosin-maleic adduct alkyd showed slight loss in gloss whereas the air-dried film showed slight blushing and considerable loss of gloss after 48 hours during water resistance test.

**Acid resistance:** Air-dried as well as baked films of all the alkyds showed good acid resistance when the films were immersed in two per cent sulphuric acid solution for 24 hours. However, only the air-dried film of rosin-maleic adduct based alkyd showed loss of gloss after 48 hours of immersion.

Table 6  
Comparison of film properties of air-dried and baked films of short oil alkyds

Sl. No.	Product	Drying time in hrs			Hardness		Flexibility and adhesion 1/4" mandrel	Impact resistance 2 lbs from 24" height	Water resistance (48 hrs)	Acid resistance (2% H <sub>2</sub> SO <sub>4</sub> )		Alkali resistance (2% Na <sub>2</sub> CO <sub>3</sub> )		Solvent resistance (MTO)	
		SD	HD	TF	Scratch (g)	Rocker (g)				24 hrs	48 hrs	4 hrs	8 hrs	24 hrs	48 hrs
<b>1. Air-dried</b>															
(i)	Rosin-maleic adduct non-phthalic alkyd	1	4	24	1400	20	P	F	3	5	3	5	0	5	4
(ii)	Maleopimaric non-phthalic alkyd	1	4	24	1700	28	P	F	4	5	4	5	1	5	5
(iii)	Conventional phthalic alkyd	1	4	24	1300	16	P	P	4	5	4	5	0	5	4
<b>2. Baked</b>															
(i)	Rosin-maleic adduct non-phthalic alkyd				1550	25	P	F	4	5	5	5	0	5	5
(ii)	Maleopimaric non-phthalic alkyd				1850	34	P	F	5	5	5	5	1	5	5
(iii)	Conventional phthalic alkyd				1400	20	P	P	5	5	5	5	0	5	4

5 = Film practically unaffected  
4 = Slight loss in gloss  
3 = Slight blushing and loss of gloss

2 = Heavy blushing and complete loss of gloss  
1 = Partial film lift off  
0 = Complete film lift off

P = Pass (ie no cracking or detachment of film)  
F = Fail (ie slight cracking of film)

**Alkali resistance:** With two per cent sodium carbonate solution none of the films (air-dried or baked) showed any effect of alkali attack in the first four hours. However, after eight hours immersion, the films of alkyds based on rosin-maleic adduct and phthalic anhydride were completely lifted off whereas the film of maleopimaric acid based alkyd showed only slight lifting.

**Solvent resistance:** All the alkyd films showed good solvent resistance in MTO even after eight hours immersion. Only slight loss in gloss was observed for the air-dried films of alkyds based on rosin-maleic adduct and phthalic anhydride.

### Short oil alkyds

Table 5 shows the general characteristics of short oil alkyds of the three types prepared above. All the alkyds had acid value in the range of 20-30. The acid value of rosin-maleic adduct alkyd was the lowest at 22.4, while that of maleopimaric and phthalic alkyds were 26.6 and 27.5, respectively. The viscosity of 50 per cent solution in xylene was the lowest (0.5 poise) for alkyd based on rosin-maleic adduct, while for alkyds based on maleopimaric acid and phthalic anhydride, the viscosity was 1.6 and 1.5 poises, respectively. The colours of all the alkyds were, however, quite close to each other.

The film properties of the short oil alkyd resins are given in Table 6.

**Drying time:** The results show that all of the alkyd films surface dried in one hour, hard dried in four hours and became tack-free in 24 hours.

**Scratch hardness:** Both the air-dried and baked films of maleopimaric acid based alkyd showed the highest scratch hardness of 1700 and 1850g, respectively. The phthalic-alkyd films, on the other hand, showed the lowest scratch hardness of 1300 and 1400g, respectively. An overall improvement in the scratch hardness of films can be observed in the baked films.

**Rocker hardness:** Maximum rocker hardness of the films was found to be 34 in case of baked film of maleopimaric acid based alkyd and the lowest at 16 in case of air-dried film of phthalic alkyd. Again, it was a general observation that the baked films possessed a greater rocker hardness as compared to the air-dried films.

**Flexibility:** All the alkyd films (air-dried and baked) passed the flexibility test on a 1/4 inch mandrel.

**Impact resistance test:** The impact resistance test indicated slight cracks in the films (both air-dried and baked) of the rosin-maleic adduct and maleopimaric acid based non-phthalic alkyds. But at the same time, the air-dried and baked films of the phthalic-alkyd passed the impact resistance test.

**Water resistance:** Air-dried films of alkyds based on maleopimaric acid and phthalic anhydride showed only slight loss in gloss when kept in water for 48 hours but rosin-maleic adduct based alkyd films showed slight blushing in addition to the loss of gloss. No effect of water was observed in baked films of alkyds based on maleopimaric acid and phthalic anhydride while only slight loss in gloss in the rosin-maleic adduct based alkyd was noticed. Thus the

baked films of all the short oil alkyds showed marked improvement in water resistance.

**Acid resistance:** The acid resistance of the baked films in all the cases was good as no adverse effect was observed even after 48 hours. However, in case of air-dried films, although no effect was observed in 24 hours, slight loss in gloss was observed after 48 hours in case of air-dried films of maleopimaric acid based alkyd and phthalic-alkyd. The loss in gloss was greater (accompanied by slight blushing also), in the case of rosin-maleic adduct based alkyd film.

**Alkali resistance:** The air-dried as well as baked films of all the alkyds showed good alkali resistance up to four hours immersion. However, after eight hours of immersion, the effect of alkali became more apparent. The air-dried and baked films of alkyds based on rosin-maleic adduct and phthalic anhydride showed complete film lift off, whereas maleopimaric acid based alkyd films showed only partial lifting.

**Solvent resistance:** The solvent immersion test during the first 24 hours showed no effect on air-dried as well as baked films of all the three alkyds. However, after 48 hours immersion, both air-dried as well as baked films of the conventional phthalic-alkyd and air-dried films of rosin-maleic adduct based alkyds lost slight gloss. All the other films were totally unaffected.

### Conclusions

Taking an overall view of the results discussed above it can be concluded that the films of non-phthalic alkyds based on maleopimaric acid, irrespective of the oil lengths, showed high scratch hardness and rocker hardness values than the films of other alkyds. On the other hand, the films of conventional alkyds based on phthalic anhydride showed poor scratch hardness and rocker hardness values. This behaviour can be attributed to the functionality and molecular size differences between the maleopimaric acid and phthalic anhydride, and molecular weight difference between two types of alkyds. Higher functionality would lead to greater cross-linking which in turn, would increase the hardness of the resin films. The film hardness increases with the increase of molecular weight of the resin.

Maleopimaric acid based alkyds (long, medium and short) also possess better alkali resistance than conventional phthalic alkyds which can be attributed to the fact that maleopimaric acid based alkyds would have a greater cross-linked structure than the phthalic anhydride based alkyds. Moreover, the presence of one sterically hindered carboxylic group in the maleopimaric acid can also provide high hydrolysis resistance to the film. The other properties of the alkyd films, such as flexibility, water resistance, acid resistance and solvent resistance are of the same order for all the alkyd types.

The results of the film properties of non-phthalic alkyd resins conclusively prove that the non-phthalic alkyd resins have tremendous scope and potential for utilisation in the surface coating industry because of their improved film properties over the conventional phthalic alkyds. Maleopimaric acid shows good potential as a raw material for non-phthalic alkyd resins and can be obtained from rosin-maleic adduct in good yields.

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## References

1. Encyclopedia of Polymer Science and Technology, Vol. 12, Interscience Publishers, New York, 1st Ed., 1970, 145.
2. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 17, Interscience Publishers, New York, 2nd Ed., 1968, 489.
3. Loeblich, V. M., Baldwin, D. E., O'Conner, R. T., and Lawrence, R. V., *J. Am. Chem. Soc.*, 1955, **77**, 6311.
4. Ruzicka, L., Balas, F., and Villim, F., *Helv. Chem. Acta*, 1924, **7**, 458.
5. Kohler, J., *J. Pract. Chem.*, 1942, **85**, 534.
6. Bacon, R. G. R., and Ruzicka, L., *Chemistry and Industry*, 1936, 546; *cf. Chem. Abstr.*, 1936, **30**, 6357.
7. Sandermann, W., *Ber.*, 1941, **74B**, 154; *cf. Chem. Abstr.*, 1941, **35**, 3263.
8. Loeblich, V. M., Baldwin, D. E., and Lawrence, R. V., *J. Am. Chem. Soc.*, 1955, **77**, 2823.
9. Arluzov, B. J., *Gen. Chem.*, 1932, **2**, 806; *cf. Chem. Abstr.*, 1933, **27**, 2688.
10. Kalnins, A., and Dobelis, J., *Latv. PSR Zinat. Akad. Vestis*, 1969, **5**, 54; *cf. Chem. Abstr.*, 1969, **71**, 49188.
11. Halbrook, N. J. and Lawrence, R. V., *J. Am. Chem. Soc.*, 1958, **80**, 368.
12. Harris, G. C., U.S. Pat., 2,517,563, Aug. 8, 1950 (To Hercules Powder Co.)
13. Smirnova, E. B. and Paderin, V. Ya., *Sintetich. Produkty iz Kanifoli i Skipidara*, Akad. Nauk Belorussk, SSR, Tsent. Nauchn. Issled i Proekth. Instn. Lesokhim. Prom., Tr. Vses. Nauchn-Tekhn. Soveshch. Grki., 1963, **77** (Pub. 1964) (Russ); *cf. Chem. Abstr.*, 1965, **62**, 14925.
14. Silver, R. P., U.S. Pat. 2,522,586, Sept 19, 1950.
15. Balkrishna, R. S., Sastry, G. G. R., and Murthy, B. G. K., *Proceedings of 32nd Annual Convention and Symposium of Oil Techno. Assoc. of India*, 12 and 13 Feb. 1977.

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## next month's issue

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

**Surface preparation for painting new galvanized structural steel** by K. G. Mottram and F. M. Petchell

**An investigation into the effect of pore size in a lacquer coating on the underfilm coating** by K. R. Gowers and J. D. Scantlebury

Together with three short communications from exhibitors at the Surfex 86 exhibition.

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## Wet Adhesion

Sir,

Due to my late cognizance of P. Walker's letter on "Wet Adhesion"<sup>1</sup> my answer is somewhat delayed. At least some of the publications mentioned in Walker's letter have been known to me and I have appreciated his work several times<sup>2-6</sup>. Walker has tried to justify, that the direct pull-off test is useful for measuring wet adhesion of organic coatings on metals, whereas I recommended the adhesive tape test for this purpose until a better test is available<sup>7</sup>. Though not being fully satisfied with the tape test either, we prefer it to the direct pull-off test for the following reasons, some of which have been mentioned by Walker<sup>8</sup>.

Under normal atmospheric conditions cyanoacrylate adhesives need about one hour for complete cure at room temperature and not just 5-15 sec<sup>9</sup>. This adhesive may penetrate into the film, and in the case of thin films even to the support, thus changing the film structure and adhesion. Moreover, as water is consumed by the curing reaction, the coating area below the attachment may become depleted of water. The most serious argument against the direct pull-off test, however, is that the time elapsed between removing the samples from the exposure equipment and pulling the specimen (according to Walker 4 hours and 15-30 min respectively between bonding and pulling off<sup>8,9</sup>) is probably too long. Water normally evaporates from a coating very quickly<sup>5,10</sup>.

Walker has measured wet adhesion both at 100 per cent r.h. and with totally immersed samples. At comparable exposure times (e.g. 50 hours) adhesion dropped to a much lower value on total immersion. Obviously both conditions have not been equivalent, and this raises the question, whether under this condition real wet adhesion was measured.

Unfortunately Walker did not indicate the scatter of the results in the totally immersed samples. In our experience with the direct pull-off test the scattering is quite significant, which agrees with what Walker's experiences with the "Humidity and Condensation Conditions" experiments.

The optical distinction between adhesive and cohesive failure is a problem, especially with dry samples. However, it is reasonable to assume that on exposure the interaction with water, by which adhesion is reduced, rupture takes place in the polar adhesion zone. We are presently trying to find out whether this assumption may be supported by ESCA—and Auger spectroscopy.

Considering the complex testing procedure of the direct pull-off test, even taking into account the recently standardized version for dry conditions<sup>11</sup>, and the restriction imposed on measuring wet adhesion, the adhesive tape test is much simpler for this purpose and not less reliable.

In our immersion experiments at 23°C in distilled water the exposure time was extended by up to two weeks until the coating could be torn off by the tape<sup>7</sup>. A few coating systems resisted the tape test even after this time. Contrary to this, Walker used an immersion time of only 50 hours.

Of course, the time after which a coating can be torn off from its support is not equivalent to the loss of adhesion, i.e. complete delamination, but it signifies a state of reduced adhesion which is probably identical with Walker's "residual adhesion". In our terminology good wet adhesion means, that this state of reduced adhesion is not attained during the exposure time chosen.

According to our observations the state of reduced adhesion always precedes blistering and underrusting. It is therefore a prerequisite for any characteristic, i.e. non-incident coating defect related to corrosion.

Walker has amply discussed<sup>8</sup> how this state of residual adhesion may be envisaged. In any case the presence of a continuous aqueous phase at the coating/metal interface must be assumed. Only then electrochemical reactions are possible at the coated metal surface. It is for this reason that I consider good wet adhesion as the primary criterium for corrosion protection by organic coatings. Cathodic and anodic areas at the metal surface can only operate if they are connected by an aqueous electrolyte and this excludes adhesion at these areas.

The onset of corrosion after the state of reduced adhesion is attained, depends on other parameters, such as: the time of exposure, the presence of electrolytes at the interface, the diffusion rate of reactants and reaction products through the coating and the presence of anticorrosive pigments or inhibitors.

The influence of these parameters may well explain why organic coatings may still protect against corrosion—even in the state of reduced or residual adhesion.

To explain why corrosion takes place when organic coatings still show good wet adhesion is more difficult. Taken for granted that really wet adhesion was measured and that, according to Walker, adhesion on mild and stainless steel should not be different, the classification of the protective quality by so-called corrosion scales may be the source of error. Usually this classification does not distinguish between corrosion defects characteristics to the support and defects due to film application and formation. Assuming that a coated panel of 8 x 10 cm<sup>2</sup> after exposure exhibits a few blisters; are they characteristic of the coating type or just a consequence of some local defects of film application? The corrosion scale does not take this into account and thereby hides some important information.

Walker has referred to his long term adhesion studies on multicoat systems<sup>9,12</sup> and concluded that no relation exists between adhesion and corrosion protection. The adhesion data given in these papers, however, are certainly not those of wet adhesion, to which I have referred. The practical exposure conditions of Walker's studies were rural and relatively free of atmospheric pollutants, i.e. not very corrosive. Comparing the steel and aluminium panels, the fluctuations of data, observed and explained by different humidities, also occurred in opposite directions at the same time. Obviously other variables, perhaps such of the measurement, have been super-imposed.

These critical remarks do not lessen the importance of

Walker's result that adhesion of many organic coatings is severely reduced by the influence of high humidity or liquid water. However, his statement, that "the resistance of a coating against the adhesion reducing the influence of water is just one factor in the mechanism of protection and perhaps even a minor one", cannot be followed, neither on a critical judgement of his data nor from our own experimental evidence.

The common statement, that many factors are involved in corrosion protection by organic coatings is neither satisfactory nor helpful to the progress of knowledge. Not at least for practical reasons we must know the order of precedence of these factors and how they are related to each other. Otherwise the stagnancy of knowledge in this field of coatings technology will not be overcome.

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Germany*

*Yours faithfully  
W. Funke*

*15 January 1986*

## References

1. Walker, P., *JOCCA*, 1985, **68** (12), 319.
2. Funke, W., *J. Coat. Technol.*, 1983, **55**, 31.
3. Funke, W., *Farbe und Lack*, 1983, **89**, 86.
4. Funke, W., *JOCCA*, 1979, **62**, 63.
5. Funke, W., Zatloukal, H., *Farbe und Lack*, 1978, **84**, 584.
6. Funke, W., *Werkstoffe und Korrosion*, 1969, **20**, 12.
7. Funke, W., *JOCCA*, 1985, **68**, 229.
8. Walker, P., *Official Digest*, 1965, 1561.
9. Walker, P., *JOCCA*, 1969, **52**, 516.
10. Funke, W., *Fette, Seifen, Anstrichstoffe*, 1962, **64**, 714.
11. DIN 53232
12. Walker, P., *JOCCA*, 1974, **57**, 241.

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## occa meetings

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### Midlands Section

#### Smectite clays and their effect on pigment rheology

The second lecture this session of the Midland Section was held on the 21 November 1985 at the Clarendon Suite, Stirling Road, Edgbaston, Birmingham.

Members and guests heard Dr R. Schwindt of NL Chemicals Limited give a talk on "Smectite clays and their effect on Pigment Rheology".

Dr Schwindt said that rheology was the science of flow. With the aid of diagrams gave definitions for shear stress and shear flow and from these derived the definition for viscosity as shear stress divided by shear flow. Because viscosity is dependent on time and temperature it is best to consider the viscosity profile of liquid. Plots of shear stress versus shear rate were shown for Newtonian, Dilatent and Pseudoplastic systems and the characteristics of each explained.

Additives control all aspects of viscosity, sagging, levelling, suspension and application and although it is possible to graph the ideal rheological behaviour for a paint in all its stages from manufacture to curing, the perfect additive is not yet available.

The speaker said that Smectite was a rather complicated name for a range of organo-clays found in various parts of the world. These exist as aluminium silicate plates carrying a negative charge due to hydroxyl ions on the edges and a positive charge due to sodium ions on the flat surfaces. They are modified by quaternary ammonium compounds to

give the desired properties of dispersability and rapid development of structure by hydrogen bonding. This bonding takes place between resin and solvent groups and not just between platelets.

Dispersion requires high shear and the addition of a polar material which aids separation of the agglomerated plates into discrete units.

In conclusion Dr Schwindt said that modern organo-clays have greater plate separations, which, by careful choice of organic groups in the quaternary ammonium compound, enable them to be dispersed without the need for high shear and polar solvents.

The interest shown in the talk was reflected in the numerous questions that were asked. The meeting closed finally with a vote of thanks proposed by Mr D. Penrice thanking the speaker for a clear and concise talk.

*B. E. Myatt*

### Newcastle Section

#### Amino resins for use in surface coatings

The third meeting of the 1984/85 session was sponsored by BIP and Mr Bob Barratt gave a lecture on "Amino resins for use in Surface Coatings".

Historically, the first amino resin patent (Oct 1920) revealed a range of possible uses for resinous condensation products of formaldehyde with various amino compounds. The inclusion of alcohols (etherification), which opened up

far wider application, was not patented until 1929: thereafter, significant development and usage had to wait for commercial availability of materials such as butanol, urea, melamine, isobutanol, methanol and benzoguanamine over the period 1936-63.

The chemistry of amino resins is based on the versatile reactivity of formaldehyde. Mr Barratt briefly sketched the condensation with urea to form methylolureas followed by their cross-linking condensations to form hard, brittle resins. He showed how control of cross-linking through inclusion of various alcohols gives resins with greater flexibility and compatibility and how methanol makes water-thinning possible. Almost half the volume of amino resin usage is in wood products as an adhesive and moulding applications account for a large fraction. Only 10 per cent of output is for coatings applications; plasticised with traditional esters and blown oils, or with reactive hydroxyl-containing polymers such as alkyds, epoxies, acrylics and saturated polyesters.

The resins have been developed and continually tailored to meet new coating needs, always as the cross-linking agent for other film-forming materials. In addition, environmental pressures have necessitated the production of resins with much lower free-formaldehyde content. Mr Barratt illustrated the effect of degree of etherification on resin/paint properties—increased stability, degree of polymerisation, compatibility, gloss, flexibility: reduced viscosity, reactivity and hardness. Specialised techniques enable good compatibility and flexibility to be achieved together with high reactivity and hardness.

The lecture was concluded with a survey of improvements in methylated melamine resins. In comparison with the earlier butylated/isobutylated types, they have wider compatibility and are more cost-effective in producing high solids/high performance coatings; with water miscibility, if necessary. Much of this is due to the smaller molecular size of methanol versus butanols allowing greater cross-link density and much lower alcohol volatiles loss during cure.

Questions afterwards covered free formaldehyde content and possible EEC labelling, loss of compatibility at very high etherification levels, necessity for some acidity with alkyds, the benefits of benzoguanamine in coating performance, aminos as flow-aids in epoxies and retardation of alkyd paint dry on chipboard.

The Chairman, Mr R. G. Carr, gave the vote of thanks for a very interesting lecture.

*J. Bravey*

## Manchester Section

### Metallic pigments

On Monday 11th November, 160 members and guests of the Manchester Section attended a sponsored lecture at the Valley Lodge Hotel, Wilmslow.

The lecture, entitled "Metallic pigments, their

manufacture and use in printing inks, paste and liquid", was given by Dr Denis Cleaver, Technical Director of Wolstenholme Bronze Powders Ltd. Bolton.

Dr Cleaver was introduced to the meeting by Mr Ian Nicholson, Area Sales Manager, and was ably supported by a team of experts from Wolstenholme Bronze Powders.

Dr Cleaver explained the misnomer in the name Bronze Powders, pointing out that the products with which we are familiar are all brass alloys of copper and zinc with a touch of aluminium. In a brief history of Bronze Powders he outlined the developments from the work by Furth in Bavaria through the development of Bessemer in England to the present Wolstenholme Bronze Powders company.

The size, shape and nature of the surface of the individual flakes was discussed along with their effects on the final optical appearance of the ink. The mechanism of light reflectance at the metal surface was explained and the effect of the alloy composition on the hue of the reflected light.

The importance of leafing of the flakes in the ink film was explained along with the factors controlled by the flake maker and ink maker which can affect this property.

Dr Cleaver went on to outline the manufacturing process of Bronze Powders dealing in some detail with the factors in the process which affect the suitability of the final product for various outlets. In particular the particle size of the finished powder is of importance in the final outlet.

The physical chemistry of the flakes in ink films was discussed with respect to the wetting of the flakes by the vehicle and the effects on flotation and rheology.

The lecture was followed by an extensive question time during which the points raised by the audience were ably fielded by Dr Cleaver and his technical colleagues.

Thanks to the generosity of Wolstenholme Bronze Powders Ltd., an excellent buffet was provided and enjoyed by all present.

A vote of thanks to Dr Cleaver was proposed by Mr Mike Nixon of the Manchester Section Committee, whose efforts in organising this lecture contributed to the success of the evening.

*R. G. Handley*

## Ontario Section

### The psychology of colour

The Ontario Section of the Oil and Colour Chemists' Association met on Monday, 11 November 1985, in conjunction with the Toronto Society for Coatings Technology, at the Cambridge Motor Hotel.

Mr Aurelian Guillory, interior design consultant, spoke on "The Psychology of Colour". His talk centered around

how colour can work for one in creating a psychologically supportive environment. A presentation was made of basic types of colour schemes and how they can help solve architectural problems with colour alone. He discussed Luscher tests and his adaptations to help determine personal schemes. The subject was discussed with reference to home and work environments, and to corporate "re-imaging".

## Varnishes for the ink industries

The Ontario Section of the Oil and Colour Chemists' Association met on Wednesday, 11 December 1985, at the Cambridge Motor Hotel, with members and guests attending in spite of the first major snowfall of the season.

Mr Chris Sevauskas, Product Manager for Vehicles, of Lawter International, Northbrook, Illinois; spoke on "Varnishes for the Ink Industry".

Mr Sevauskas traced the development of varnishes, from the early combinations of a bodied vegetable oil with a rosin component, to later systems for web fed, heat set, offset with press speeds of 700 feet per minute. He then noted more recent advances in gelling and chelating agents which allow the use of press speeds of 2200 feet per minute yet provide leveling for good gloss, and good dot formation. Further improvements in these agents have been able to reduce misting. The use of new materials to meet regulatory requirements promised new developments in the near future.

A lively question and answer period followed in which many expressed their personal viewpoints on recent regulations. The speaker was thanked by Mr Purnell, the Chairman.

*P. Marr*

## Transvaal Section

### Paint additives

On Wednesday, 29 May, 1985, Mr Hein Scheepers of Rohm and Hass addressed the Section on the subject of Paint Additives.

#### *Rheology Modifiers/Thickeners*

A brief description was given on the developments that have taken place in this field. The difference between rheology modifiers and thickeners were outlined, i.e. rheology modifiers change a portion of the viscosity/shear rate curve, do not build viscosity along the remainder of the curve, and are used in conjunction with thickeners. Thickeners change the entire viscosity/shear rate curve, and can be used alone.

Formulating techniques and the use of these products were outlined highlighting features and benefits.

#### *Dispersants*

The emergence of a new family of polyacrylic dispersants

was outlined, that gives the paint manufacturer versatility across a wide range of PVC, low foam, low millbase viscosity at greatly reduced costs compared to previously available dispersants.

#### *Opaque Polymers*

The use of opaque polymer as an opacifier in Trade Sales paints was discussed.

The opaque polymer which consists of a hollow resin sphere contributes to hiding in paints by allowing better utilisation of titanium dioxide, and also through more efficient light scattering as a result of its constitution. Utilising opaque polymer give the formulator two options: (a) increase paint performance properties at equal cost and (b) reduced formulated cost at equal paint properties.

Following question time and a vote of thanks proposed by Mr Jan de Jong, the members and guests enjoyed the generous hospitality of Rohm & Hass (Pty) Ltd.

### Mini symposium

On Wednesday, 19 June, 1985, the Section meeting took the form of a Mini Symposium at which four young speakers were invited to talk for ten minutes on the theme "Trouble Shooting in the Paint Industry".

Alan Dewsnyp, a Resin Chemist with AECI Paints, discussed a problem involving the preparation of identical Epoxy Amine Adducts at two different factories. Product of the required low viscosity could not be reproduced when manufactured at the second plant. Initial investigations showed no variation in reaction conditions or raw materials used. However, it was discovered that the Polyamine used was supplied to one plant as prills and to the other in flake form.

Laboratory work showed that the flakes dissolved faster in the liquid epoxy resin, giving off heat at a greater rate which caused quicker reaction with resultant higher viscosity. The problem area had therefore, been identified and the polyamine in its original form is being used and production is back to normal.

Marlene King is a production engineer in the Body and Trim Shop at BMW South Africa. Her talk dealt with the concepts of problem solving and trouble shooting, and the methods used to implement these concepts. A methodical scientific approach is necessary to explore, define and analyse the cause of the problem, prior to the development and adoption of possible solutions. The speaker closed her talk by stressing the benefits and incalculable value of efficient, planned trouble shooting, particularly in production line situations.

Ian Nicholson, a raw material manufacturer's representative from Lewis and Everitt, spoke on the trials and tribulations of importing raw materials. He explained the methods of indenting and shipping and examined the pitfalls of shipping delays, customs hold-ups forward cover, and terms of payment. After discussing the advantages and disadvantages of ex-stock versus direct indent purchases,

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the speaker ended his address with an appeal for understanding that raw material suppliers have their fair share of trouble shooting, often of an intangible, frustrating, bureaucratic nature, unrelated to product quality or performance, yet they remain cheerfully committed to customer satisfaction as a challenge to be constantly faced and met.

Howard Rayner, a technical service chemist with Hoechst (SA), discussed an approach to the solution of deviation problems, which are most likely due to a change in materials used, equipment used, method, human actions, or extraneous influences. Analysis of these factors usually provides a starting point from where corrective action may begin. The speaker then related a case history whereby a coating which had been used successfully for several years had a sudden failure. The customer complained that a textured coating cracked badly and firmly believed that the resin emulsion was the cause of the problem. Laboratory investigation showed that both the emulsion and the coating were within specification and that no other complaints had been received about that particular batch of emulsion. Further investigation of possible deviation revealed that a change in coalescent and a sudden cold snap during application, had combined to cause the failure.

A vote of thanks was proposed by Mr Peter Gate, who congratulated the speakers on their objectivity in their approach to problem solving, and expressed that hope that more functions of this nature would be forthcoming, to encourage active participation in OCCA by the younger members.

### Corrosion protection within a mining group

This talk was presented to the Section on 24 July by Dr

Alan Rose, head, materials engineering, Gencor Group Laboratory Services.

The present economic climate is compelling the mining industry to become more aware of the materials that it uses. In an inflationary environment, there is the temptation for companies to lift prices to counter rising costs. The gold industry is not able to do this and must look to improvements in economies and productivity to meet the present crisis. These are achieved by better use of materials, being more cost-conscious and by getting better value for money in all areas of its activities. Such an approach includes getting longer life from plant, machinery and structures; and this in turn involves better design, operating standards, choice of materials and protection.

In the past, materials problems have traditionally been handled by the engineering departments. This is not unnatural since they have often been responsible for design, construction and erection of plant. Their interest and involvement is understandable. As a result of this situation paint specifications have originated in the engineering departments after consultations with the paint suppliers, and painting or corrosion consultants.

Since 1981 Gencor has had within its Technical Services Division the Materials Engineering Department (MED) whose scope of activity includes material selection and the use of protective coatings, be they metallic, organic or paint systems.

Following an enlightening discussion period, the speaker was thanked by Mr Dirk Pienaar.

B. Bailey

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## conference discussions

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Discussion is encouraged at OCCA Conferences following the presentation of papers. Those who put the questions were asked to fill in discussion slips with the details of their questions. Edited versions of the discussions that followed the paper published in the **February 1986** issue appears below: questions in ordinary roman type, answers in italic. Only those questions for which discussion slips were received are published.

### Effect of titanium dioxide pigments on the cure of thermosetting films

#### T. Entwistle

N. REEVES: The presence of zinc oxide on titanium dioxide has been related to good durability. In view of the adverse effects of zinc oxide on some systems, are you suggesting that high durability pigments cannot be used with these systems?

T. ENTWISTLE: *The durability of titanium dioxide pigment depends upon two factors. Firstly the photocatalytic stability of the crystal and secondly the effectiveness of the coatings of inorganic oxides precipitated onto the surface of*

*the crystal. In the early days of rutile titanium dioxide production it was found that addition of zinc, before calcination, was very effective in producing a stable crystal and, as the addition was relatively simple, the majority of grades rated as durable or highly durable contained zinc. However, over the years, replacements for zinc have been found which are equally effective. In addition, the techniques used in precipitating the inorganic coatings have improved, thereby improving the durability of the resultant pigment. Consequently the use of zinc to produce durable or highly*



durable grades is no longer necessary and indeed it is fairly safe to say that the majority of new grades (introduced since about 1970) are zinc free.

D. SCANTLEBURY: With reference to the second table which appeared on page 31 of February 86, *JOCCA* and your data on the daily variation of  $T\alpha$  and hardness values; could this be explained by the variation in relative humidity?

T. ENTWISTLE: Pendulum hardness values are undoubtedly affected by temperature and humidity and using a glass plate as a "standard" does not eliminate these variables. We are not certain how  $T\alpha$  is affected by temperature and humidity but the results given on page 31 (second table) suggest that the effect on  $T\alpha$ , if any, is much less than on pendulum hardness.

D. SCANTLEBURY: With reference to Figure 21, does the insulating film contribute to  $\tan \delta$  values?

T. ENTWISTLE: The insertion of the insulating film (Figure 21) will affect the values of capacitance and conductance and as

$$\tan \delta = \frac{G}{C2\pi f}$$

then  $\tan \delta$  will also be affected. However we have assumed that these effects will be constant and we are primarily interested in the differences in  $T\alpha$  for different paint films.

H. FOSTER: In the case of powder coatings have you compared the results of dielectric analysis with DSC measurements, and if so, did you find any correlation between the two methods for assessing the degree of cure?

T. ENTWISTLE: We have not yet compared results of dielectric analysis with DSC measurements but the powders mentioned in Table 5 are being evaluated under a sponsored project at a UK university and such comparisons will be available in due course.

C. SCHOFF: I would like to comment on the use of DSC to follow and characterise cure; we, at PPG have had very little success using DSC to study the cure of conventional (liquid) coatings, but find that the technique is quite useful for powder coatings, especially epoxy systems?

T. ENTWISTLE: We have carried out a limited amount of DSC work to characterise the cure of powders but we have found that interpretation of the curves can be difficult in some instances. We are hopeful that dielectric analysis will provide an alternative method and the first indications are promising. The values for  $T\alpha$  are very reproducible and generally the interpretation of the curves is much less ambiguous than DSC. The equipment will also probably be cheaper.

S. T. HARRIS: In the early days of polyester/epoxy powder coatings development, a system was patented which relied upon the presence of zinc oxide to catalyse the

core. This system was never commercially accepted due to inconsistent results with various batches, and I suspect this was due in part to the differing spreads of molecular weights. It may be beneficial to compare the effect of zinc oxide against the glass transition temperature ( $T_g$ ) and the effect on this  $T_g$  variation of the cured film in DSC analysis.

T. ENTWISTLE:  $T\alpha$  is obviously related to  $T_g$  and both in the paper and in my presentation I have shown how  $T\alpha$  for the cured film can be affected by the presence of zinc oxide. Also in the paper, but which, due to time constraints, I omitted from the presentation, there is a section on an alternative use of dielectric analysis with powder coatings. This allows  $T\alpha$  to be measured as the powder is cured. Hopefully, when the work being carried out at the University (as mentioned in an earlier answer) is completed we will be able to correlate  $T\alpha$  and  $T_g$  both for powders and the cured films.

D. S. NEWTON: From the bar graphs it would appear that interactions between the zinc oxide, alumina and silica, are possible. Have you considered the possibility of normal statistical analysis to determine the presence (and significance) of these interactions?

T. ENTWISTLE: When using commercial pigments there are probably too many unknown variables to be able to isolate the required interactions of zinc oxide, alumina and silica. However, statistical analysis should be possible with those paints and powders where we have used experimental pigments. The work to date has suggested that further experimental pigments using only increasing amounts of either aluminium or silica rather than mixtures would be very helpful and we intend to pursue this.

A. ZAKARIA: Is the dielectric analysis instrumentation commercially available, and is it computer interfaceable?

T. ENTWISTLE: I understand that a suitable Dielectric Analysis Instrument is commercially available in the USA but is fairly expensive. We assembled our apparatus from readily available laboratory equipment e.g. a Wayne Kerr Autobalance Universal Bridge B642; a Stanton Redcroft linear temperature programmable oven and an x-y-t recorder (not necessary if you are prepared to take readings of capacitance (C) and conductance (G) at 30 second or 60 second intervals). The only equipment we had to make ourselves was a suitable "jig" for clamping the paint film (applied to a metal panel) between two suitable electrodes, the bottom electrode containing a thermocouple. The jig was then placed inside the oven. We will be pleased to demonstrate our method or to provide drawings to anybody interested in making their own equipment.

As the instrument is in effect given values of C and G to enable

$$\tan \delta = \frac{G}{C2\pi f}$$

to be calculated at different temperatures from which  $T\alpha$  (i.e. the temperature at which  $\tan \delta$  shows a maximum) is calculated, the method is ideal for use with a computer and should eliminate the use of the x-y-t plotter.

**Export agreement for Birmingham paint company**

PPG Industries (UK), has secured a major licensing agreement to supply paint technology to the Kenyan auto assembly industry. The agreement, with Coral industries of Nairobi, gives the company access to advanced PPG technology to enable them to manufacture original automotive paint systems in Kenya.

Export Manager of PPG Industries (UK) Ltd, Michael Murtough commented, "This is a significant breakthrough into the East African market, and makes the most advanced automotive paint technology in the world—such as that supplied to UK customers including Austin Rover, Vauxhall and Ford—available to the rapidly expanding Kenyan auto assembly industry.

"By adding local manufacturing and service to PPG's proven product expertise, Coral will be in a particularly strong position to service the specialist needs of their local automotive market".

**Caldwell Paint Manufacturing Co. Inc.**

Reed International Plc has acquired, through Reed Holdings Inc., the share capital of Caldwell Paint Manufacturing Co. Inc., of St Louis, Missouri, USA. Caldwell's principal activity is the production of a specialist primer, for use in conjunction with paints and wallcoverings, which is distributed nationally across the USA.

**ICI appoint Durham Chemicals distributors**

Durham Chemicals Distributors Ltd will in future be responsible for handling orders of up to 24 drum lot size of Methylene Chloride as the official distributors for ICI Plc Mond Division. Methylene Chloride is a non-flammable solvent widely used in industries such as surface coatings, plastics, rubber and textiles as a stripping, softening or cleaning agent.

**Ransburg distributors appointed**

Ransburg UK Limited have announced the appointment of SVP Distributors Ltd, to handle all Ransburg and GEMA products in the Midlands and North-East.

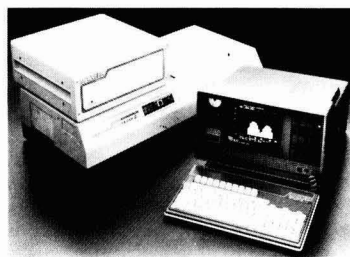
SVP, with depots in Middlesbrough and Newcastle will offer sales, service, and hire facilities throughout Cleveland and Tyne and Wear. The company is well established in the area with a field force of six sales

engineers. SVP spokesman, Peter Flegg, explained that the move into electrostatic paint-spray and powder-coating equipment had been dictated by customer demand. Both on- and off-shore sectors of the region's traditional heavy industry were looking to preserve margins in the face of much increased competition. The reduction in waste that resulted from switching to electrostatic methods was highly significant. As Peter Flegg put it: "When you think of what it takes to cover the hull of a ship or an oil rig, a 30 per cent to 40 per cent saving is a lot of paint!"

**Berger sells Canadian Cuprinol company**

Berger and Hoechst Canada, joint owners, have sold Cuprinol Korzite Ltd of Guelph, Ontario. The rights to use the Cuprinol trade mark and to manufacture and sell Cuprinol products in Canada have been acquired by Sico of Montreal, the major Canadian coatings company.

Sico and Cuprinol UK will continue to work together within a royalty and technology agreement.



The Malvern Autosizer IIc

plotter package for sophisticated data presentation.

The complete Autosizer IIc package is designed for true ease of use with user-friendly software and simple function key operation. Typically, a complete analysis is said to take less than 30 seconds and may require as little as ten.

*Reader Enquiry Service No. 30*

**New cobalt pigments for plastics and paints**

Degussa AG of Germany, has added four new cobalt pigments for plastics and paints to its range of inorganic coloured pigments. The new items are the blue pigments 5050, 5100 and 5200, which have a greenish to reddish tinge, and the green pigment 6060, with a yellowish tinge. Compared with the standard pigment grades (5001 blue, 5002 blue and 6001 green) the new pigments are notable for their increased covering power and improved colour intensity. Infra-red examination has shown them to be suitable for camouflage paints as well.

*Reader Enquiry Service No. 31*

**Mercury-free biocides**

Riedel de Hæen AG, a member of the Hoechst Group of Companies, and manufacturers of the Mergal range of industrial biocides have announced that in future all of their biocides will be mercury-free.

Because of the dangers of associated with organo-mercurials, and their persistent effects in the environment, Riedel de Hæen will it has been claimed concentrate on using only the safer but equally effective new generation of organic active ingredients.

Mergal products such as Mergal K6N for in-can preservation, Mergal BCM for blue-stain prevention are already mercury-free

products

**Submicron particle sizer**

The introduction of the Malvern Autosizer IIc is said to bring new speed and performance capabilities to submicron particle size analysis.

It uses the technique of photon correlation spectroscopy to measure particles from three nanometres to three microns in materials such as micelles, polymer latexes and microemulsions. Fully detailed, high resolution results are obtained for all types of size distribution whether narrow or broad, single—or multimodal. Diffusion coefficients and polymer molecular weights can also be measured.

In the Autosizer IIc, the analyst has for the first time all the power of a full 8-bit, 72-channel correlator and a 16-bit computer giving optimum data resolution and data processing capabilities. The Malvern Multi-8 correlator also incorporates Variable Time Expansion (VTE), using up to four different auto-correlation sample times per analysis to give greatly enhanced data quality compared with that obtainable from a linear correlator. Accessories include a laser electrophoresis module for zeta potential measurement and a graphics

and have established themselves in the market place. New products such as Mergal S89 for algicidal protection are also mercury-free. The Mergal biocides are sold in the UK by Hoechst (UK) Ltd.

Reader Enquiry Service No. 32

**Mixers are right for the American market**

Joshua Greaves and Sons Ltd, manufacturers of industrial mixers, have been making rapid progress with regards to the American market during the past few months.

Following the receipt of their largest single order to date from the States (for heavy duty turbine agitators) the company recently flew the flag at the prestigious New York Chem Show '85 Exhibition, where over 600 companies displayed products to a recorded 5,800 visitors from the process chemical industries.

Greaves shared the stand with Jayco Inc., their Mahwah, New Jersey-based American agents, and demonstrated their advanced V. GM 5 high-shear and in-line high-shear mixers, together with the popular family of Greaves Laboratory Mixers.

Held at the New York Coliseum on December 9-12, 1985, the show was the 41st of its kind, and enabled Greaves to not only secure around 60 very positive leads in America, but also to hold preliminary talks with the Chinese Chamber of Commerce, who showed interest in their products.

Reader Enquiry Service No. 33

**New coating system**

A highly flexible coating system designed for internal walls and ceilings in public areas has been introduced by Glixtone Ltd of Birmingham. The Spectrum-G wall coating system is said to allow both a textured and flat multi-coloured finish, offering vandal-proof surface protection, as well as a highly decorative finish. The

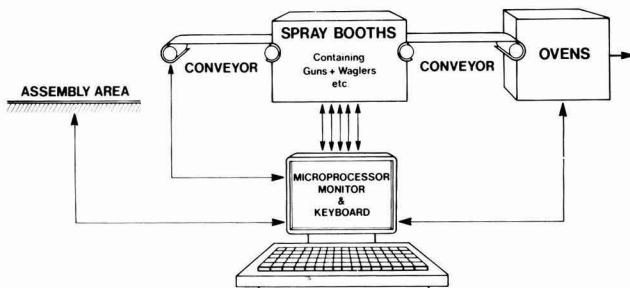
**Microprocessor control of spraying operations**

A new system for masterminding the control of spraying operations, Spray-Tech, is available from IGG Techsystems Ltd. It is based on the company's Vutec monitor coupled with Intel microprocessor or IBM computer. Spraying jobs, it is said, can now be easily programmed via a standard terminal keyboard, with jets operating on an XY grid.

Spray-Tech is linked via sensors and controllers into the total spraying system, ie controlling choice of booth, conveyor speed, gun position, and status of electrostatic, fluid bed, filter, material/air, and dilution/forward air.

Operation is *via* means of a video monitor and input keyboard, housed in a control panel. The microprocessor will hold a choice of individually prepared programmes for instant call up, each tailored to a specific series of spraying sequences. These govern all operations, from entry of product onto conveyor, including movement of guns and wagglers, through to storage and sprayed product in drying ovens. Supervision can be restricted to the control console, which can be programmed to sound audible warnings if any operation functions imperfectly.

Reader Enquiry Service No. 34

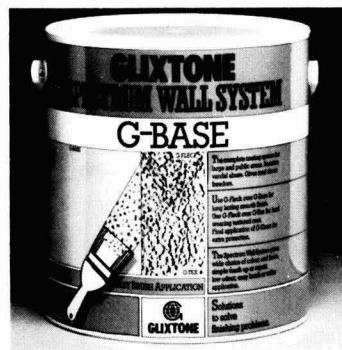


Spray-Tech, the microprocessor controlled spraying system

system comprises G-Tex texture coating, and a finish of either G-Glaze clear coat, or G-Flek brush applied glaze, giving a durable and decorative coating.

G-Base is a washable, odourless, non-combustible coating with anti-static and anti-fungal properties. It is available in a range of mixable colours, which can be brush, roller or spray applied. G-Glaze is a clear coat which can be applied over one layer of G-Tex to give a soft mono glaze, or over spattered G-Tex to give a decorative surface which is virtually impossible to write on. G-Flek is a washable brush-applied glaze with flecks of colour suspended in it.

Reader Enquiry Service No. 35



The Spectrum-G wall coating system

**meetings**

**Basics of colour**

A short course of lectures and demonstrations on "The Basics of colour" will be held at UMIST from the 23-25 April, 1986. This mid career training course will cover the basic principles of

colour physics and colour measurement and its content will include colour vision, absorption and reflection, colour mixing and reproduction, fluorescence, metamerism, the relation between reflectance and colorant concentration, colour spaces, the CIE System, colour measurement and colour differences.

The course is said to be relevant to employees in the paper, printing, textile and paints industries or anyone interested

in the science of colour. Accommodation will be available on campus and places on the course will be limited to 20. The course fee is £140 which is inclusive of lunches. Further details and an application form are available from: The Director of Communications, UMIST, PO Box 88, Manchester M60 1QD.

**Cellucon 86**

A conference on wood and cellulose will

take place at Wrexham from July 14-18, 1986. Part of the industrial section of the conference will be devoted to surface coatings. Further information can be obtained from the Conference Secretariat, Research Division, The North East Wales Institute, Deeside, Clwyd CH5 4BR.

### Printing inks for packaging

The Manchester Section of OCCA will be holding a two-day symposium entitled "Printing Inks for Packaging—Recent Changes, Future Trends", at the University of Salford on Thursday and Friday, April 10-11, 1986.

A poster exhibition/display is featured, a symposium dinner and overnight accommodation are optional extras. Copies of the brochure are available from Mr M Nixon, Winnetts Inks Ltd, Demmings Works, Brookfield Road, Cheadle, Cheshire SK8 2PR. Tel: 061-428 8521, telex: 665089. *The closing date for applications is Thursday, March 27, 1986.*

### BPVLC symposium

The Birmingham Paint, Varnish and Lacquer Club will be holding a symposium on "Management and investment required to achieve coatings laboratory efficiency—miracle". This will be held at the Strathallan Hotel, Hagley Road, Birmingham, on Thursday, May 22, 1986, commencing at 10 am.

### Symposium on Health and Safety

The London Section of the Oil and Colour Chemists' Association are holding a one-day symposium entitled "Health and Safety in the Coatings and User Industries". This will be held at the Royal Institution, London W1, on Thursday, 10 April, 1986, commencing at 10 am with coffee being available from 9.30 am.

The meeting will be of interest to Production and Laboratory Managers because of their responsibility for ensuring safe working conditions for their workers as well as to Health and Safety Officers who are directly involved.

The programme will include information on the toxicity of raw materials, labelling for supply and conveyance, and risks of fire and explosion. Prominently featured will be the implications of the control of Substances Hazardous to Health Regulations with speakers from Paintmakers' Association and the London School of Hygiene and Tropical Medicine.

For further information contact:

Mr K. H. Arbuckle, Berger Group, Freshwater Road, Dagenham, Essex RM8 1RU. 01-590 6030.

### Coatings Science 1986

Two short courses on the science of coatings will be presented at North Dakota State University this summer. The first course from June 2-6, 1986, is on "High-solids and Radiation Curable Coatings", and the second course from June 16-27, 1986, will be on "Coatings Science". For further information contact the Division of Continuing Studies, Room 212, Ceres Hall, PO Box 5819, University Station, Fargo, North Dakota 58105, USA.

## literature

### New contour cabins for component finishing

A four page A4 colour leaflet has been produced by Paint and Powder Systems Ltd, on their new range of contour cabins for the component finishing industries. The contour cabins illustrated have been subjected to several years development for use with electrostatic powder spraying processes and recovery plant. They are designed and manufactured to a UK patent and are claimed to offer considerable advantages over conventional equipment including good air control, quick and easy colour changes, together with space, energy and powder savings. They also comply with all known European safety regulations for use anywhere within the workshop.

Several varieties of contour cabins are described in the literature to cover any scale of component finishing application. Small batch production in trade coating workshops with manual operation can be offered, together with high volume throughout as part of a continuous production line including a high degree of colour change options if required.

To complement the range of contour cabins, several filtration and powder recovery systems are illustrated. These include change filters with either intermittent or continuous cleaning cycles, together with cyclone filtration incorporating powder sieving and collection hoppers. Paint and Powder Systems also offer a complete plant layout and product design service incorporating full manufacturing facilities covering all aspects of component finishing equipment.

Reader Enquiry Service No. 36

### New products brochure

The most recent developments in a wide range of instrumentation produced by Kent Industrial Measurements, a Brown Boveri Kent company, are shown in a full colour illustrated brochure now available on request. The brochure describes how, by the use of up to the minute technology, Kent have introduced a whole new range of microprocessor based instrumentation, a family of transmitters and converters and a series of new flowmeters and liquid and gas analysers.

Reader Enquiry Service No. 37

### New literature from Valentine

Valentine has introduced four new brochures covering its Valroc, Valflash, Spragloss and Fleet paint systems respectively. Each brochure folds out into a wall chart providing refinishers with a step-by-step guide on the use of the systems. With the aid of a colour coded chart the Valroc, Valflash and Spragloss brochures are said to provide comprehensive information on every stage of the painting process from the use of preparation products, such as primers and fillers, through to the application of top-coat and clear lacquer. This includes specific information on which products to use together in order to maximise the benefit of the entire system.

Reader Enquiry Service No. 38

## people

**Michael Hancock**, BSc, MSc, MIOP, has been appointed Director of Pira's Printing and Information Technology Division, as from February 1, 1986.

★ ★ ★ ★

**Michael Palmer** has been appointed to head the newly created Aqueous Coatings Laboratory at Scott Bader. A graduate in Physics, Michael has ten years experience in aqueous coatings technical service. Most recently he served as a section leader at Vinyl Products.

Official Guide to

**SURFEX**  
86

will appear in the  
APRIL issue

## Annual General Meeting 1986

The 1986 Annual General Meeting of the Association will take place at the Unicorn Hotel, Prince Street, Bristol, and will be preceded by a Reunion Luncheon to which Past Presidents, Past Honorary Officers and Honorary Members of the Association are invited as the Association's guests.

Following the Luncheon an illustrated talk will be given by a speaker from the *SS Great Britain Project* which will deal with the work of restoration and the problems of corrosion involved in this important project.

This talk has been arranged by the Bristol Section of the Association and it is felt that members of the Association will be most interested in the talk on this project, and those visiting Bristol for the AGM may like to take this opportunity to go and see the *SS Great Britain* on the same day.

The Unicorn Hotel has agreed on a special rate for any member attending the AGM wishing to stay overnight either on Tuesday 17 or Wednesday 18 and those wishing to avail themselves of this facility should write to the Unicorn Hotel, stating that they are attending the Association's Luncheon Lecture in order to obtain the preferential rate.

Forms of application for the Luncheon will be sent to members with the 1985 Annual Report in May *JOCCA*.

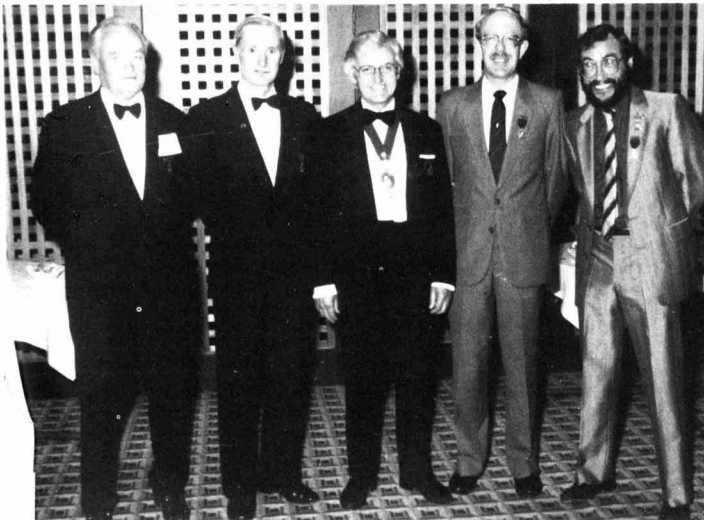
Provided there are sufficient members wishing to participate it may be possible to arrange a guided tour of the *SS Great Britain* at 10.00 am on the morning of the AGM (Wednesday, 18 June 1986) and applications for the visit should be made at the same time as application for luncheon tickets. However, members travelling from abroad who wish to participate but would not receive the May issue in time should write to Priory House as soon as possible indicating that they would like to take part in the tour and/or luncheon; details will then be sent to them in May by air mail.

## New Zealand Division

### Badge Presentation

In the October 1985 issue of *JOCCA* (p273) a report appeared on the presentation of special lapel badges to commemorate service as both Vice-Presidents and Chairmen of the Divisions, together with a photograph of the South

African presentation. We are pleased to publish here a photograph showing the presentation made to the past Chairmen of the New Zealand Division which took place at the Rotorua Convention in July 1985. Absent from the photograph were Mr R Bettison (Vice-President 1981-83) and Mr R Spargo (current Vice-President).



the presentation made at the 23rd New Zealand Convention, Rotorua, July 1985, from left to right are: Mr T Slinn (Vice-President before Division formation), Mr Willis (Vice-President 1983-85), Mr F Redman (President OCCA), Mr P Sharp (Vice-president 1977-79), Mr C Gooch (Vice-President 1979-81).

## SURFEX 86

Readers will be aware that the new concept exhibition for the surface coatings industries organised by the Association (known as SURFEX 86) will be held at Harrogate in May 1986 and all space in Hall D, reception and gallery areas has been reserved.

The exhibition, which takes place at the Harrogate Conference Centre, Yorkshire, England, will be open on the following dates and times:

Wednesday 14 May 1986 09.30 - 18.00 hrs.

Thursday 15 May 1986 09.30 - 17.00 hrs.

On the first evening the West Riding Section of the Association is arranging a Dinner to take place at the Hotel Majestic, Harrogate, and a considerable number of tickets have already been sold. Details have been printed in the members' monthly bulletin and non-members wishing to apply for tickets (£16 each inclusive of VAT) should apply to Mr. G. C. Alderson, c/o Sandoz Products Ltd., Calverley Lane, Horsforth, Leeds LS18 4RP (Tel: 0532 584 646).

The following hotels in Harrogate have offered special rates for exhibitors and visitors to SURFEX 86. Those wishing to avail themselves of this facility should state clearly that they are attending/visiting SURFEX 86 when booking accommodation:

Old Swan Hotel  
Granby Hotel  
The Cairn Hotel  
The Gables Hotel  
Adelphi Hotel  
Askern Guest House

The *Official Guide* to SURFEX 86 will be printed in the April issue of *JOCCA* and will also be freely available at the entrance to the Exhibition. Admission will be free.

Advertising in the April issue will not be confined to exhibitors and other companies/organisations wishing to have details of these facilities should contact Priory House as soon as possible.

The full list of exhibitors is published elsewhere in this *Journal*.

Prior to the exhibition the Paint Research Association will be organising a seminar in Harrogate at the Cairn Hotel on the 12 and 13 May on the subject "Coatings for plastics".



## Natal Section

### Dinner Dance

The 1985 Annual Social function of the Natal Section took the form of a Dinner/Dance on Friday, 30 November 1985 at the Durban High School Old Boys Club.

Again the paint manufacturers and raw materials suppliers were generous in their sponsorship but the response from OCCA members was disappointing. An excellent buffet supper with selected house wines was provided.

The keynote address was given by Mr W. M. Fowles Past President of the Natal Chamber of Industries who gave an interesting and succinct speech on the subject of communication.

The Chairman then presented a rose bowl and miniature to Ms Ilona Davies for the best lecture to the Natal Section during

the 1984/85 year. This award has been introduced as an innovation to encourage more speakers and maintain a high quality of lectures in the future. Ms Davies was a worthy first recipient of the floating trophy for her lecture in August, 1984 entitled "Modern Instrumental Techniques in the Coating Industry".

After these formalities the evening continued with dancing which was enjoyed by all.

R. H. Philbrick

Banks, W. T. (London)  
 Carlsson, B. MSc. (General Overseas—Sweden)  
 De Legge, D. J., BSc. (Ontario)  
 Gillatt, J. W., BSc. (Manchester)  
 Looi, T. C., BSc. (General Overseas—Malaysia)  
 Okeke, J. A., BSc. (General Overseas—Nigeria)  
 Spenceley, D. M. (Hull)  
 Tan, M. L., BSc. (General Overseas—Singapore)  
 Thomas, J. H. C. (Bristol)  
 Timpson, D. C. (London)  
 White, H. F. (Midlands)

### new members

The sections to which new members are attached are shown in italics together with the country, were applicable.

#### Ordinary members

Achi, S. S., PhD. (West Riding)

#### Associate members

Dunn, M. H. (Auckland)  
 Fensham, A. W. (Transvaal)  
 Rang, M. (Auckland)  
 Vickers, C. (Transvaal)

#### Registered student

Ripley, C. J. (West Riding)

Reprints of articles and papers in JOCCA are now available

If interested, Tel: 01-908 1086

CLASSIFIED ADVERTISEMENTS

## R & D OPPORTUNITIES IN NORWAY



JOTUN

Jotun is a worldwide organisation for production and sale of polymers, paints and coatings of which Jotun Marine Coatings (J.M.C.) is a part, responsible for the sale and product development of High Performance Coatings worldwide. J.M.C. has its own plants or licence production in more than 20 countries in all parts of the world. The central research laboratory of Jotun and J.M.C. is situated in Sandefjord, Norway, in a modern, well-equipped location.

J.M.C. wants to strengthen the research and development teams and therefore has openings for:

### SENIOR CHEMIST/PROJECT MANAGER AND RESEARCH CHEMIST

#### Senior Chemist/Project Manager

This position requires an M.Sc. or Ph.D. degree in chemistry and 5-10 years' experience in the paint industry or similar. The responsibilities will include project development and research in modern coating technology and technical responsibility for new projects. The candidate will stay in close contact with suppliers of raw materials as well as Research Institutes. They will also co-operate with our International Marketing Manager in marketing new products worldwide, with lecturing in such connection. The position will consequently include travelling worldwide.

#### Research Chemist

This position requires an M.Sc. degree in chemistry and experience in the paint industry. The candidate will work as part of the research team on applied research and development of all kinds of modern high performance coatings and technical assistance projects. The ability of independent work, creativity and co-operation are required.

Should you require further information in the first instance please contact: Mr. N. Scotland, Managing Director, Jotun Henry Clark Ltd, 6-8 Fenchurch Buildings, London EC3M 5HU. (Tel: 01-481 2741).

The appointments provide excellent career opportunities in an expanding international company, competitive salary and free life insurance. Modern laboratory working conditions in an area with excellent year-round sports and summer water sports, camping, hiking and fishing.

Please send a detailed C.V. and salary requirements in confidence to: Personnel Department Jotun A/S, P.O. Box 400, N-3201 Sandefjord, Norway.

# JOCCA

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This enquiry will be forwarded to the company/ies concerned.

### JOCCA

Priory House, 967 Harrow Road, Wembley,  
Middx., HA0 2SF, England  
Telephone: 01-908 1086 Telex: 922670 (OCCA G)

Photocopy or cut out form and send to above address:

## SERVICES

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- \* COUMARONE-INDENE RESINS – liquid
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Tel. 0634 401448. Telex 966147 TAMS G



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For details concerning this and other services available, including knowledgeable problem solving and product formulation give me a ring on **0623-550001**.

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## SITUATIONS VACANT



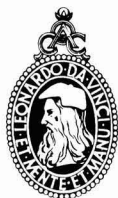
### COATES BROTHERS PLC

#### PAINT TECHNOLOGIST

Cray Valley Products, a leading resin manufacturer located at Farnborough, Kent, require an experienced paint technologist to work on R & D projects associated with coating systems in decorative and industrial paints.

Apply to:-  
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Coates Brothers PLC,  
Waterloo Works,  
Machen,  
Newport,  
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# OIL & COLOUR CHEMISTS' ASSOCIATION



## NEW PUBLICATION SPECIAL ANNOUNCEMENT MONOGRAPH SERIES — NO. 2 NOW AVAILABLE FROM ASSOCIATION'S OFFICE, BY PREPAYMENT ONLY.

**Water-borne coatings** by J. W. Nicholson, BSc, PhD, CChem, MRSC, Laboratory of the Government Chemist.

Basic principles of water-borne coatings — the nature of water — principles of solubility/dispersability in water — emulsions and dispersions — electrodeposition — principles of electrodeposition — polymers for electrodeposition — the change from anodic to cathodic electrodeposition — pigmentation of paints for electrodeposition — emulsion paints — film formation by emulsion paints — polymers for emulsion paints — formulation of emulsion paints — latex paints for corrosion protection — gloss emulsion paints — recent developments in water-borne coatings — developments in water-soluble resins — developments in cross-linking reactions — flash-rusting inhibitors — aqueous powder coatings.

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Please send ..... copies of Monograph 2 **Water-Borne Coatings** at £7.50 each (surface mail) (US \$18.00)

I enclose remittance for £..... (**prepayment only**)

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1500 gallon titanium half-coiled jacketed reactor; 300 gallon Pfaudler glass-lined reactor A series; 225 gallon stainless steel jacketed reactor; 45 ph Silverson stainless steel mixer 1460 rpm, flameproof; 20 hp 750 rpm Kottoff stainless steel mixer type MS5; 10 hp Keenomix change pan mixer; 5.5 hp Silverson Flashmix 2880 rpm; Cowles dissolver type 510VHV, 10 hp, flameproof; Cruickshank 45 gallon stainless steel bowl mixer; Gardner u-trough mixer, mild steel, 110 cu. ft.; Jenkins u-trough mixer, stainless steel, jacketed, 30 cu. ft.; Vrieco mixer type S, mild steel, 140 cu. ft.; Nautamix stainless steel 200 litre type M18652; Mitchell 4 cu. ft. stainless steel double cone drier; Calmic 6 tray vacuum drier, stainless steel, model C51; Penwalt Sharples vibro screen 69 ins. dia.; Russell Turbo Finex, stainless steel, model A14077; GVS stainless steel decanter centrifuge 7.5 hp, model K120; Krauss Maffei 24 in stainless steel basket, type V4A/E; Kalix Dupuy paste filling machine type KX60; Alexanderwerk powder compactor type 150; Head Wrightson stainless steel pan granulator; Alkyd resin plant, 1 ton capacity.

## PILOT PLANT:

10 litre reactor, stainless steel, for hydrogenations; 15 litre reactor, stainless steel, with condenser; OVF climbing film evaporator; Meta Filter, stainless steel, 5 sq. ft. pre-coat type; Calmic 20 cm dia. stainless steel pressure filter; Alfa laval 6 in. dia. pusher centrifuge model SB160; Alfa Laval and APV plate heat exchanger, small; Manesty Petrie fluid bed drier model 10E; Hobart bowl chopper and mincer, lab. size; Hunt 2 litre stainless steel z-blade mixer; Glen Creston model 5300 laboratory grinder; Vacuum pumps, variety.

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## OIL & COLOUR CHEMISTS' ASSOCIATION

# SURFEX 86

Exhibition of the latest developments in raw materials and equipment used in the manufacture of paints, printing inks, colour, adhesives and allied products to be held at

Harrogate Exhibition Centre,  
Yorkshire, England.  
Wednesday, 14 May, 1986  
09.30-18.00 hrs  
Thursday, 15 May, 1986  
09.30-17.00 hrs

Admission Free

The "Official Guide" will be printed in the April 1986 issue of the Association's Journal (JOCCA) and will be freely available at the entrance to the Exhibition.

**Oil & Colours Chemists' Association,  
Priory House,  
967 Harrow Road,  
Wembley, Middlesex, HA0 2SF,  
England.**

**Tel: 01-908-1086. Telex: 922670 OCCA G.**

# SURFEX 14th-15th May 1986 86 Harrogate Conference Centre

## List of Exhibitors

Allied Colloids Ltd  
Samuel Banner Ltd  
Baxenden Chemical Co  
Blythe Burrell Colours Ltd  
Boud Marketing  
BP Chemicals Ltd  
E. P. Bray & Co Ltd  
Bromhead & Denison/Teikoku Kako Co Ltd  
Buckman Laboratories Ltd  
Byk Chemie GmbH  
CIBA GEIGY Pigments  
CIBA GEIGY Plastics  
Cornelius Chemical Group Ltd  
Cray Valley Products  
Croda Colours Ltd  
Croxton & Garry Ltd  
Diamond Shamrock UK Ltd  
Durham Chemicals Ltd  
ECC International Ltd  
Eiger Engineering Co  
Elektro-Physik  
Ellis & Everard  
Ernstroem Minerals AB  
Floridienne UK Ltd T/AS Micro Products  
Foscolor Ltd  
Fuel & Metallurgical Journals Ltd  
John Godrich Consulting Engineers  
H. Haeffner & Co Ltd  
Haeffner Machinery Ltd  
Harlow Chemical Co Ltd  
Heracus Equipment Ltd  
Heubach UK Ltd  
Hoechst UK Ltd  
ICI Organics Div  
Kenroy Dispersions  
Kirklees Chemicals Ltd  
Kirstol Ltd  
K & K Greeff Ltd  
Lawrence Industries Ltd  
Marlow Chemicals Ltd  
Mastermix Ltd  
Metal Box Ltd  
Miox Ltd  
3M UK Plc  
NL Chemicals UK Ltd  
Norwegian Talc  
Paintmakers' Association  
Paint Research Association  
Pearson Panke  
Perchem Ltd  
The Q-Panel Co Ltd  
Red Devil Inc  
Reed Plastic Containers Ltd  
Resinous Chemicals Ltd  
Sandoz Products Ltd  
SCM Chemicals Ltd  
Scott Bader & Co Ltd  
Seaton Group (Microfine)  
Shear Chemicals Ltd  
Sheen Instruments L5d  
Shell Chemicals UK Ltd  
Silberline Ltd  
C & W Specialist Equipment  
Steeley Minerals Ltd  
Tego Chemie Service  
Tioxide UK Ltd  
Torrance & Sons Ltd  
Union Camp Chemicals Ltd  
Vuorikemia Oy  
Wengain Ltd