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**JOURNAL OF THE
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Theories—laboratory investigations—practical performance

B. Lindberg

The theory and practice of film formation by co-ordination reactions involving aluminium compounds

J. H. W. Turner, P. Womersley and W. K. H. Lakin

Practice makes perfect

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FOR TRAVEL ARRANGEMENTS TO ALEXANDRA PALACE SEE MAP ON PAGE xvii

TRAVEL ARRANGEMENTS

Since the Association's last Exhibition at Alexandra Palace, travel arrangements have been improved by the addition of the Victoria Line to the Underground system, which now links Victoria Station to the Piccadilly Line at Finsbury Park. The building of the extension of the Piccadilly Line from Hounslow to the Airport terminal at Heathrow is now well advanced and when this is completed in due course it will give a direct link with Turnpike Lane Station on the Piccadilly Line. In the meantime a bus service operates from Heathrow Airport to Hounslow West Station. Those travelling by the Piccadilly Line should alight at Turnpike Lane Station and the Association will be running a bus shuttle service from this station to and from Alexandra Palace. The journey from central London to Turnpike Lane takes approximately 18 minutes.

Reproductions are available of the two-colour map shown on page xvii. Members of the Association may obtain copies by sending a stamped self-addressed envelope, marked "Alexandra Palace map" in the top left-hand corner, to the Association's offices at the address on the Contents page opposite

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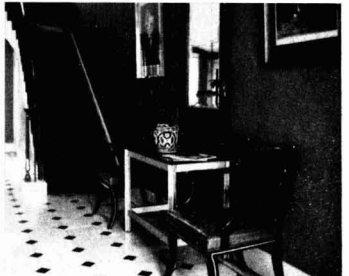
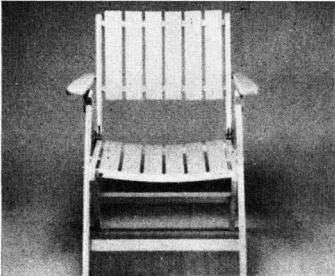
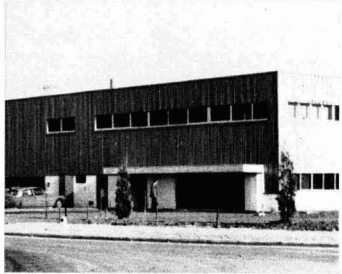
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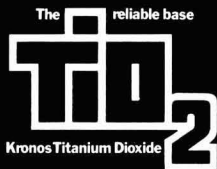
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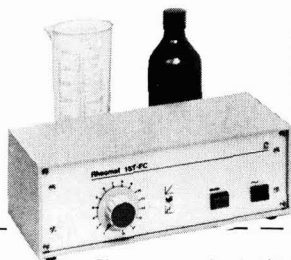


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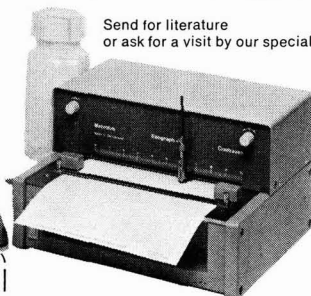


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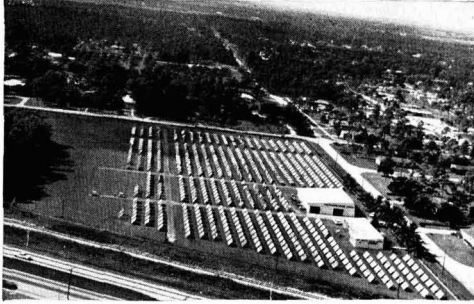
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JOURNAL of the OIL AND COLOUR CHEMISTS' ASSOCIATION

Hon. Editor: S. R. Finn, BSc, FRIC, FTSC

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Vol. 58 No. 11

November 1975

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Theories—laboratory investigations—practical performance*

By B. Lindberg

Scandinavian Paint and Printing Ink Research Institute, Odensegade 14, 2100 Copenhagen, Denmark

Summary

Some problems concerning the relationship between theoretical aspects and practical performance of painted surfaces are critically examined. In order to correlate theory with practice different laboratory methods and measurements are needed. The selection of realistic and correct methods for this evaluation is very important and the question of correlation is often dependent on the measuring method employed and the criteria chosen. The problems discussed in the text are based upon investigations of the weathering of paint films and the painting of plastics.

Changes in paint film performance during outdoor exposure and in

Keywords—Part 1

Types and classes of structures or surfaces to be coated:

aluminium

Raw materials:

binders (resins, etc.)

acrylic emulsion
alkyd resin
chlorinated rubber
fluorocarbon resin
urethane resin

prime pigments and dyes

titanium dioxide

Equipment primarily associated with analysis, measurement or testing

indentation hardness tester
weatherometer

Keywords—Part 2

Types and classes of coatings and allied products

acrylic coating
alkyd coating
epoxy coating
nitrocellulose coating
rubber base coating
urethane finish
vinyl coating

Type and classes of structures or surfaces to be coated

plastic

the laboratory have been followed and compared by measuring gloss, weight loss, tensile strength, elongation, micro-indentation hardness, whiteness and by taking photographs with a scanning electron microscope. With regard to the painting of plastics, some theories concerning the relationship between the adhesion and the surface tension of the two components have been studied. The adhesion was measured by the pull-off method and the surface tension by contact angle measurements. The results reveal the complexities and difficulties which arise when endeavouring to obtain correlation between theory and practice.

Processes and methods primarily associated with:

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accelerated weathering

service or utility
film degradation

Properties, characteristics and conditions primarily associated with:

materials in general
elasticity
tensile strength

dried or cured films

chalk resistance
gloss retention
weather resistance

Properties, characteristics and conditions primarily associated with materials in general

adhesion
contact angle
interfacial tension
surface tension
wettability

Théories—études de laboratoire—rendement dans la pratique

Résumé

On fait une étude critique des problèmes à l'égard du rapport entre les aspects théoriques et le comportement des surfaces peintes dans la pratique. Afin d'établir une corrélation entre la théorie et la pratique on a besoin de diverses méthodes et mesures de laboratoire. La sélection des méthodes rationnelles et aptes à cette évaluation est très importante et la question de la corrélation se dépend très souvent de la méthode utilisée et des critères choisis. Les problèmes que l'on discute dans le texte se basent sur les investigations du vieillissement de feuillets de peintures et sur le peignage des matières plastiques.

Les changements du comportement des feuillets de peintures au

cours de l'exposition et à l'extérieur et au laboratoire ont été étudiés et comparés par les mesures du brillant, de la perte de poids, de la résistance à la traction, de l'allongement, de la dureté par micro-indentation, de la blancheur, et par les prises de vue au moyen du microscope électronique à balayer. Au sujet du peignage des matières plastiques, on a étudié certaines théories à l'égard du rapport entre l'adhérence et la tension superficielle à l'aide des mesures d'adhérence au moyen du ruban adhésif, et à l'aide des mesures de l'angle de contact dans le cas de la tension superficielle. Les résultats démontrent les complexités et les difficultés mises en évidence au cours de tentatives à établir une corrélation entre la théorie et la pratique.

*Paper presented at the Association's Biennial Conference held at the Grand Hotel, Scarborough, Yorks, England, from 17 to 21 June 1975.

Theorien—Laboratoriumsuntersuchungen—Verhalten in der Praxis

Zusammenfassung

Die Beziehungen zwischen theoretischen Gesichtspunkten und dem Verhalten in der Praxis bei gestrichenen Oberflächen auftretenden Probleme werden kritisch geprüft. Um eine Korrelation zwischen Theorie mit Praxis herzustellen, braucht man Laboratoriumsmethoden und Messungen. Die Wahl realistischer und richtiger Methoden für diese Bewertung ist höchst wichtig, und die Frage der Korrelation hängt häufig von der benutzten Messmethode und den gewählten Kriterien ab. Die im Text besprochenen Probleme beruhen auf Untersuchungen der Bewitterung von Lackfilmen und der Lackierung von Kunststoffen.

Veränderungen im Verhalten von Anstrichfilmen bei Bewitterung

Introduction

One fundamental task for a paint research institute is to study and explain all imaginable properties of paint films and how these are influenced by a number of internal and external parameters. When all the factors involved are working together, very complex phenomena occur. From his experience and knowledge, the paint scientist attempts to put these phenomena into defined terms and explanations in the form of equations and theories. The usefulness and correctness of such theories must be checked, of course, for correlation with practical measurements or experience.

In most experimental work usually only one parameter is studied at a time, whilst all the others are held more or less constant. Consequently, rather limited information is obtained because the interaction between parameters changing simultaneously (as in practice) is not taken into consideration. In the practical testing of paint properties, although carried out under so-called "controlled test" conditions, properties are often measured which are difficult to describe and define by theories and mathematical formulae. Typical properties of this type are adhesion, brittle point, hardness, flexibility,

im Freien und im Laboratorium wurde nachgegangen, sie wurden durch Glanzmessungen, Gewichtsverlust, Zugfestigkeit, Bruchdehnung, Mikroindentationshärte, Weissgrad und photographische/Ablastelektronenmikroskop-Aufnahmen verglichen.

Mit Bezug auf die Lackierung von Kunststoffen wurden einigen Theorien betreffend Haftung mit Hilfe von Messungen der Bandabreissmethode, und der Oberflächenspannung durch Messung des Kontaktwinkels nachgegangen. Die Ergebnisse machen klar, wie Komplex und schwierig es ist, zu versuchen, Korrelation zwischen Theorie und Praxis zu erhalten.

weather resistance, and corrosion resistance. Even more troublesome are the practical failures outside the laboratory, where there is normally very limited knowledge of the effects causing the failure. The history of the unsuccessful system is also, in most cases, unknown.

Today more and more sophisticated theories and measuring techniques are being developed for the study of paint properties. Thus the investigative possibilities are good but also very extensive. From a practical or economic point of view it is often impossible to study all conceivable parameters affecting a system. The choice of representative, but not too large an amount of material for investigation is important but difficult because in most cases some limitations must be made. With a knowledge of the many components in a paint formula and the existing substrates in different environments, it is easy to appreciate the great number of possible combinations. In order to reduce the amount of material and the number of measurements during investigations, it is important to use statistical methods for planning and evaluating the experiments. In this paper, some of the problems mentioned will be discussed and illustrated by work carried out at the Scandinavian Institute.

Part 1. Weathering of organic coatings

Theories and literature

Refs. 1-19

A very important property of paint films used outdoors is their resistance to weathering or "service life". The evaluation of this property takes a very long time when painted panels are exposed under natural weather conditions. In order to speed up the deterioration, artificial weathering machines are used in laboratories, but the question then arises what is the time correlation between outdoor exposure and accelerated ageing in weatherometers. Many research workers have written papers on this subject. One of the most comprehensive reviews has been reported by Brand and others at the Batelle Memorial Institute¹ where nearly 900 references covering the period 1921-1967 are reviewed. In this review, the subject "weathering" is considered from a broad viewpoint. A narrower review has been published by Kuentler and Shur². Among the more recent literature reviews is a highly scientific one by Sullivan³ which should be mentioned. Research in the titanium dioxide industry has been especially active in studying the weather resistance of TiO₂-pigmented paint systems and especially the "pigment" properties, such as gloss, chalking, whiteness, etc. At the 1974 FATIPEC Congress no less than six of the papers were concerned with weathering problems.

For the practical person, it is of great interest to know whether correlations exist between outdoor exposure results and experience of paint performance on the one hand, and accelerated weathering tests in laboratories on the other. From ASTM standards G 23-69 and G 26-70⁴ concerning weatherometer testing, the following paragraph (number 22) is worth quoting: "Since the natural environment varies with respect to time, geography, and topography, it may be expected that the effects of natural exposure will vary accordingly. All materials are not affected equally by the same environment. Results obtained by use of this recommended practice shall not be represented as equivalent to those of any natural weathering test until the degree of quantitative correlation has been established for the material in question."

One requirement for correlation is that the light simulate natural sunlight as closely as possible with regard, for example, to the spectral distribution and intensity. Today the best, but not complete, similarity is achieved with a xenon arc lamp with borosilicate filters. The importance of not using more ultraviolet (UV) light than in natural sunlight has been pointed out by Berger⁵. This phenomenon is especially critical for polyurethane binders, and light sources with wavelengths lower than 290nm should not be used.

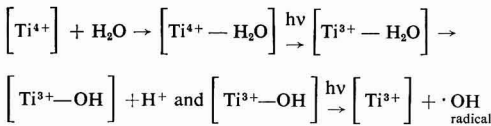
All organic material, and thus also paint binders, are sensitive to UV light. On the other hand, inorganic materials

such as mineral pigments and fillers are not at all or only very slightly attacked by UV light. Consequently, those people who use or test TiO₂ pigments have a tendency to use more strongly accelerating weathering cycles. One such cycle is the so-called "Dew-cycle", which uses unfiltered carbon arc light and dew condensation on the panels. It was first proposed by Stieg⁷ who states: "The Dew-cycle in the XW-R Weather-Ometer used in conjunction with demineralised and temperature-controlled water may be expected to duplicate results anywhere in the world." Finzel⁸ is also very positive and writes: "The Dew-cycle Weather-O-meter test has been found extremely useful in determining the relative durability of protective coatings." More critical views have been put forward, for example, by Oakley⁹: "The Dew-cycle method, although the most rapid means of promoting film degradation, has been shown to be extremely unreliable as a means of evaluating polymer performance." Some German quotations are also worth mentioning. Papenroth¹⁰ declares: "A general accelerated weathering method which is valid in all cases does not exist today and there will never be one." A more optimistic point of view concerning weatherometers is represented by Rechman and Epple¹¹ who state: "Perhaps even more reproducible results may be obtained from accelerated laboratory weathering than from the best outdoor weathering."

When using commercial weathering machines, the influence of light, water and sometimes corrosive gases is normally studied, but outdoors there are also parameters, such as temperature variations, biological degradation, wind and snow erosion, dirt pick-up etc—destructive forces which are very difficult to simulate in one weathering machine or cycle.

"Internal" factors, for example pigment volume concentration (PVC), may to a great extent influence gloss and chalking, according to Schwindt¹². Other properties which change during exposure are micro indentation hardness, tensile strength, elongation, adhesion, water permeability, surface morphology and so forth. Hardness or microindentation has been studied by Whiteley¹³ and Oesterle¹⁴. Changes in tensile strength and elongation of free films are described by Holsworth¹⁵ and Schurr¹⁶. The elongation at break especially was reduced drastically with many of the paint films investigated. Holsworth has also found that the water permeability may increase or decrease depending on the type of paint. Walker¹⁷ has demonstrated that the adhesion after nine years' exposure may vary from -58 per cent up to +815 per cent (based on the original adhesion values).

Finally two more theories or models describing the deterioration of pigmented paint films due to weathering are discussed. Changes in the properties of the paint film are primarily due to chemical processes. Völz *et al*¹⁸ have found that the degradation of the polymeric binder is initiated by hydroxyl radical formed by photochemical reactions of the titanium atoms in titanium dioxide pigment:



The tendency to initiate degradation is also dependent to a high degree on the crystal structure such as with anatase TiO₂ where chalking is much more prevalent than with the rutile grade. The tendency to chalk can be reduced by coating the titanium dioxide with special metal oxides.

An interesting geometric model for explaining the loss of gloss has been put forward by Sperry and Mercurio¹⁹. They describe a theoretical relation between loss of gloss *G* and the depth of erosion (proportional to loss of weight) based on the model shown in Fig. 1. Pigment particles assumed to be

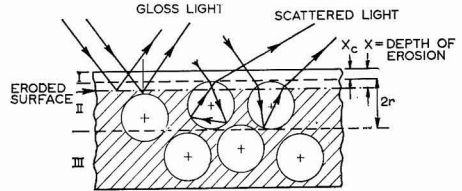


Fig. 1. Idealised paint film geometry for calculation of gloss versus erosion depth *X*. *X_c* = depth of clear layer

spherical (radius *r*) and having a volume fraction ϕ_v are distributed at random throughout the film bulk, but do not protrude through the film surface; that is, particle centres cannot approach the surface closer than $x = r$, where *x* is distance from the initial film surface. Thus, the area fraction of pigment ϕ_A in the plane $x = 0$ is zero. As erosion proceeds to a depth *x*, progressively more and more pigment area is exposed and the decrease in gloss should be some function of this exposed area. The relation of ϕ_A to ϕ_v , *x* and *r* for the interval $0 \geq x \geq 2r$ can be shown to be:

$$\phi_A = 0.75 \phi_v \left(\left(\frac{x}{r} \right)^2 - \frac{1}{3} \left(\frac{x}{r} \right)^3 \right) \dots \dots \dots (1)$$

The measured loss of gloss is assumed arbitrarily to be directly proportional to the exposed area of pigment:

$$G_x = G_0 (1 - k\phi_A) \dots \dots \dots (2)$$

where *G*₀ and *G_x* are the gloss values at $x = 0$ and *x* respectively, and *k* is a proportionality factor ($1 \geq k$) which allows for possible disruption of the binder beyond the immediate cross-section of the pigment particle. Substitution of equation (1) into (2) leads to:

$$G_x = G_0 \left(1 - 0.75 k\phi_v \left(\left(\frac{x}{r} \right)^2 - \frac{1}{3} \left(\frac{x}{r} \right)^3 \right) \right) \dots \dots \dots (3)$$

From equation 3, it can be concluded that the gloss *G_x* will decrease as the pigment volume ϕ increases, the pigment radius *r* decreases and the depth of erosion *x* increases. The paint film as shown in Fig. 1 is divided into three separate regions where the loss of gloss and of weight are changing at different rates (see Fig. 2).

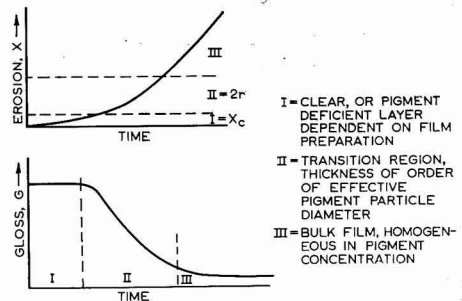


Fig. 2. Schematic diagram for erosion of TiO₂ pigmented film and relation to gloss

- I = CLEAR, OR PIGMENT DEFICIENT LAYER DEPENDENT ON FILM PREPARATION
- II = TRANSITION REGION, THICKNESS OF ORDER OF EFFECTIVE PIGMENT PARTICLE DIAMETER
- III = BULK FILM, HOMOGENEOUS IN PIGMENT CONCENTRATION

Experimental work (weathering)

The purpose of this investigation was to study and follow changes in paint film properties during natural outdoor exposure in comparison with laboratory testing with different weathering cycles. The importance and degree of change in "weathering" properties was studied by use of different techniques and measuring instruments. Another aim was to find weathering cycles which showed good correlation with different outdoor exposures. Six very different paints were exposed at three outdoor test stations and in five different weathering cycles. The following materials and procedures were used:

Paints

- A Alkyd, air drying (linseed oil alkyd 68%, "Plexal P 68 H"), PVC 25%
- C Chlorinated rubber ("Pergut S10"), plasticiser chloroparaffin 40, PVC 23%
- E Epoxy/polyamide, two-component ("Epikote 1001"/"Versamid 115"), PVC 19%
- F Commercial fluorocarbon polymer, polyvinylidene fluoride (PVF₂) ("Kynar 500")
- L Acrylic latex ("Rhoplex AC-34"), PVC 40%
- U Polyurethane, aliphatic two-component ("Desmodur N"/"Desmophen 651"), PVC 18%.

All the paints except *F* were prepared at the Institute and contained titanium dioxide (RNCX) rutile grade as pigment. The paints were applied to the substrate by use of a spiral applicator at a dry film thickness of approximately 50 to 60 μm (except paint *F* which was applied by the supplier).

Substrate

Anodised aluminium panels (20 μm oxidised layer) were used as the substrate. Some of these panels were provided with grooves on the back so that small pieces could easily be broken from the panels at certain time intervals during the period of exposure, for example, for the purpose of taking photographs with the scanning electron microscope (SEM). Tin panels were used whenever free films had to be prepared. The paint films were detached from the substrate by amalgamation of the tin with mercury.

Exposure of painted panels

The outdoor weathering tests were carried out at:

- W1: Lejre, 40km outside Copenhagen. Rural climate. Exposure period: January 1972-January 1974.
- W2: Bohus Malmön, 100km north of Gothenburg. Coastal climate. Exposure period: January 1972-January 1974.
- W3: Florida, USA (Sub-Tropical Testing Service). Subtropical climate. Exposure period: February 1972-February 1974.

The laboratory testing was carried out in different Atlas Weather-Ometer models and under various cycles. The exposure time (total time) was approximately 1 550 hours, except in the case of "Sunshine" without filter (WO6 below), where a period of only 450 hours was used.

- WO1: Xenon 6 000W, 102/18 (min. light/min. water without light), borosilicate filters, 63°C, relative humidity (RH) 40 to 45%. Weather-Ometer model 600 DMC-WRC.
- WO2: The same as WO1, but light also during the water period (in accordance with ASTM G 26-70).
- WO3: Xenon 6 000W, 60/60 (min. light/min. cold water on the back of the panels without light), type Dew-cycle, borosilicate filters, 63°C. Weather-Ometer model 600 DMC-WRC.
- WO4: Twin enclosed carbon arc, 102/18 (min. light/min. water without light), 63°C, Weather-Ometer model DL-TS (newer description DMC-W).
- WO5: Sunshine carbon arc with Corex D filters 1-2-2-6 (1 hour water without light/2 hours light/2 hours water without light/6 hours light). Weather-Ometer model XW-W.
- WO6: Sunshine carbon arc without filter, original Dew-cycle 60/60 (min. light/min. cold water on the back of the panels without light). Weather-Ometer model XW-W. Total exposure time 450 hours.

Methods of evaluation

Gloss: Measured in accordance with ASTM-D 523 with a 60° Gardner glossmeter. Panels exposed outdoors were measured before and after washing with a detergent solution (1 per cent Tween, 50°C). Panels exposed in Weather-Ometers were not washed. Exposures W1-3 and WO1-6.

Chalking: Measured in accordance with ASTM-D 659 with use of a black, soft piece of cloth drawn across the sample by hand. Exposures W1-3 and WO1-6.

Loss of weight: Determined with an analytical balance on aluminium panels weighed after storage at 50 per cent RH, 23°C for 24 hours. Panels exposed outdoors were washed before weighing. Panels exposed in Weather-Ometers were not washed. Exposures W1 and WO1, 2, 3, 5, and 6. Two panels per sample.

Micro-structure: By use of a scanning electron microscope (Joel JSM-U3) the morphological structure of the paint films after varying exposure times was studied. By scanning over the whole sample (diameter 10mm) a representative photograph of the actual sample was taken at ×700 and ×7 000 magnification. The samples were vacuum-coated, first with a layer of coal and then gold, which was found to give the best SEM-photographs. Exposures W1-3 and WO1.

Micro-hardness (indentation): Measured with an ICI micro-indentation hardness apparatus. The indentation depth *h* after 60s under a well defined load *m* was determined. The indentation needle had a radius *r* of 0.19mm. Before measurements were taken, the samples were "conditioned" under standard climatic conditions. By use of the Hertz equation:

$$E/(1 - \nu^2) = 0.75 \frac{mg}{r^{0.5} h^{1.5}} \dots \dots \dots (4)$$

the value $E/(1 - \nu^2)$ was calculated where *E* = Young's modulus of elasticity and *ν* the Poisson's ratio (a material constant varying between 0.3 and 0.5). The formula is a rough approximation derived from the ideal case of the contact

between two spherical, elastic homogenous bodies. Exposures W1 and WO1, 2, 5, 6. Five measurements per sample.

Tensile strength and elongation: These two properties were measured with an Instron tensile tester model 1026, principally in accordance with ASTM D2370-68. The cut free films were 25mm in width and the gauge length was chosen at 25mm. The elongation speed (crosshead speed) was 50mm per minute. The thickness of the tested films was measured so that tensile strength at break (MPa = N/mm²) could be calculated. The elongation was calculated at the increase in length Δl as a percentage of the original length ($\Delta l/l_0$). Exposures WO1, 2 and 3. Two determinations per sample.

Results and discussion

The original material is extensive (about 50 diagrams and 100 SEM photographs) so that the results cannot be described in detail. The conclusions drawn will be illustrated by a selected number of diagrams and photographs and the question of correlation between outdoor and laboratory weathering testing will be discussed.

Gloss correlation

Gloss is still one of the most frequently used and popular methods for describing weathering of paint films. One problem with outdoor exposure panels is the question whether or not the panels shall be washed. If the paint films show severe dirt pick-up there is a good reason for washing, but if the paint has chalked washing will drastically change the gloss of the unwashed paint (the chalk is washed off and the gloss is increased). As a matter of fact, four different gloss values can be considered, the gloss being measured on panels as indicated below:

Panels unwashed (gloss I)

Panels washed only once (at time of final inspection). One panel removed from rack at each inspection (gloss II)

Panels washed at each inspection (repeatedly). Gloss determined before (gloss III) and after washing (gloss IV).

This gives an idea of the complexity involved when discussing gloss correlations. The same type of gloss must be measured when comparing gloss values and the "unwashed" values should be preferred as representative of the "original" loss of gloss without any disturbing influence from washing. The effect of different types of washing is illustrated by the Florida exposure in Table 1.

When comparing the results, it is possible to show how the gloss changes for all six paints in diagrams for each exposure or conversely, to show how each paint performs under the different exposures (one diagram for weatherometer cycles and one for outdoor exposures). Two of the paints, namely the acrylic latex and the fluoropolymer, are not of interest as far as gloss is concerned, because they have little or no gloss. From diagrams showing the six paints for each exposure, the correlation was judged visually by four research workers at the Institute using the following scale:

- 5 = very good correlation
- 4 = good ,,
- 3 = slight ,,
- 2 = poor ,,
- 1 = very poor ,,

Gloss correlation between the six WO cycles

	WO2	WO3	WO4	WO5	WO6
WO1	5	3	4	3	1
WO2	—	3	2.5	3.5	1
WO3	—	—	4	3	1
WO4	—	—	—	2	1
WO5	—	—	—	—	1

Table 1

Gloss variations due to washing. I = gloss without washing. III and IV are gloss before and after washing every month respectively (same panel). Exposure in Florida

Paint		A	C	E	F	L	U
Unexposed		85	89	100	29	5	96
Six months' exposure	I	21	49	5	26	2	85
	III	18	53	5	26	3	87
	IV	43	63	36	28	5	93
Twelve months' exposure	I	9	32	0	25	0	70
	III	12	36	3	25	3	72
	IV	23	53	25	27	4	89
Twenty-four months' exposure	I	5	15	0	20	0	25
	III	5	22	0	20	0	30
	IV	11	38	25	23	0	35

Gloss correlation between the outdoor exposures W1-3 and the laboratory cycles WO1-6

	WO1	WO2	WO3	WO4	WO5	WO6	Σ
W1, Lejre	3	3	3	2	3	1	15
W2, B-M	2	2.5	3	2	3.5	1	14
W3, Florida	2	2.5	2.5	2	3	1	13
Points	7	8	8.5	6	9.5	3	

Gloss correlation between the three outdoor climates

	W2	W3
W1	4	3
W2	—	3

The results are mean values of the individual ratings by four assessors. To illustrate the effect of the various weathering exposures on the "gloss sensitive" paints (A, C, E and U), gloss curves are shown in Figs. 3a-b, 4a-b, 5a-b and 6a-b. From the gloss data, the following conclusions are drawn:

1. A severe exposure in a weatherometer, such as the open carbon arc without filter (WO6), with a high amount of UV light, gives poor correlation with outdoor exposures, especially for the polyurethane coating (U).
2. The best overall correlation (for all three outdoor climates) was obtained with WO5, but the difference between the six WO-cycles is, in fact, relatively small, except for WO6 and to some extent for WO4.
3. Xenon lamp exposure with borosilicate filters (WO1 and WO2) gives somewhat faster deterioration compared with the twin enclosed carbon arc (WO4).
4. No accelerated break down of the paint films was achieved by spraying cold water on the back of the panels WO3 (compare total exposure hours between WO2 and WO3). The degradation seems to be more sensitive to UV light than to water (comparing WO6 with WO3).
5. With low gloss paints (for example, the acrylic latex and fluoropolymer paints), gloss measurements give no indication of film breakdown; their gloss changes very little, or not at all, during exposure. Other methods, however, clearly prove that the acrylic latex is deteriorated.
6. The chlorinated rubber paint gave the largest deviations (Figs. 4a-b) in gloss for different exposures. The reason for this may be that the levelling of the chlorinated rubber paint was not very good and a flat homogenous film was not formed.
7. Compared with the two Scandinavian climates, the Florida deterioration is much more severe, especially for the epoxy and the polyurethane paints. The loss of gloss is about twice or three times as fast in the Florida climate.
8. The best correlation of the outdoor exposures with the WO-cycles was found to be given by the exposure at Lejre (W1). The ranking of the paints was correct for all three outdoor exposures.

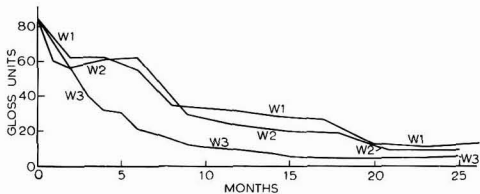


Fig. 3a. Gloss of alkyd paint (A); outdoor exposure

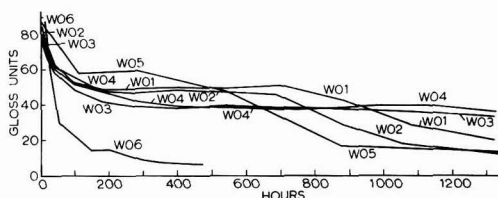


Fig. 3b. Gloss of alkyd paint (A); weatherometer, total exposure time

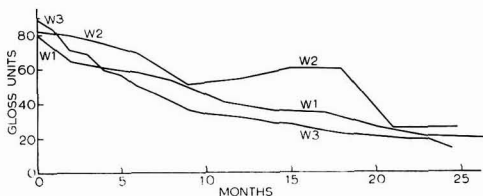


Fig. 4a. Gloss of chlorinated rubber paint (C); outdoor exposure

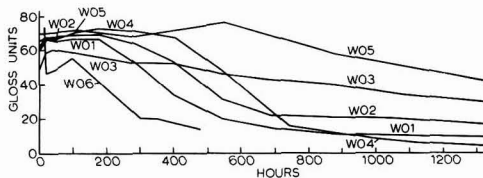


Fig. 4b. Gloss of chlorinated rubber paint (C); weatherometer, total exposure time

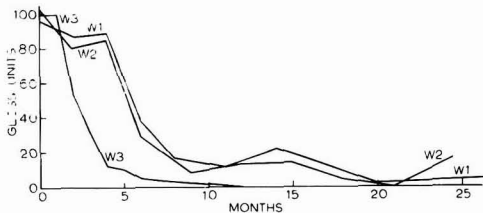


Fig. 5a. Gloss of epoxy paint (E); outdoor exposure

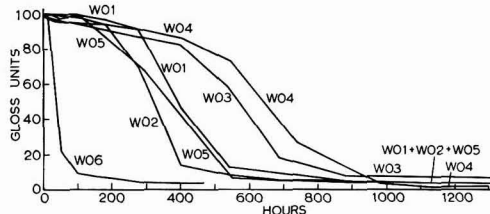


Fig. 5b. Gloss of epoxy paint (E); weatherometer, total exposure time

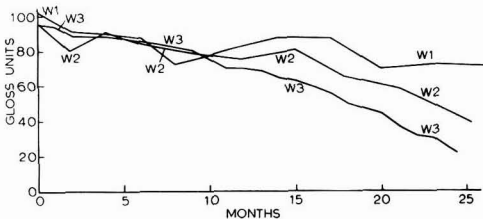


Fig. 6a. Gloss of polyurethane paint (U); outdoor exposure

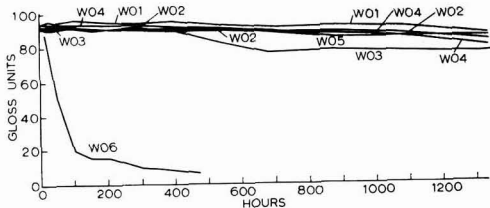


Fig. 6b. Gloss of polyurethane paint (U); weatherometer, total exposure time

Weight loss correlation

During the exposure to light (UV) and water, the binder in paint films is chemically degraded and the more resistant inorganic pigments and fillers are gradually exposed. This phenomenon is described as "chalking". In order to check that the aluminium substrate does not corrode, an unpainted aluminium panel was exposed outdoors (Lejre). The change in weight of this panel was very small, namely an increase of 13mg during one year of exposure.

The loss of weight in the different exposure climates was compared in the same way as for gloss:

Loss of weight correlation

	WO1	WO2	WO3	WO5	WO6
W1	2	2	2	2.5	2
WO1	—	4.5	2.5	3.5	2
WO2	—	—	2	3	2
WO3	—	—	—	2	1
WO5	—	—	—	—	1.5

Quite a different picture of the weathering durability was obtained by this method compared with gloss measurements. To illustrate the type of curves, Fig. 7 (W1) and Fig. 8 (WO1) are shown. From the investigation the following conclusions can be drawn:

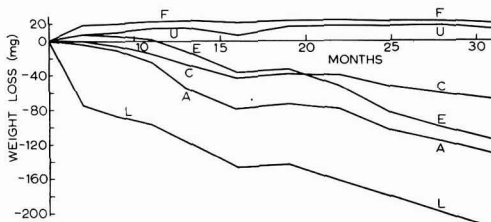


Fig. 7. Loss of weight, outdoor exposure in Lejre; panel size 7.5 x 23cm

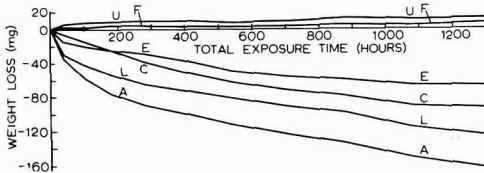


Fig. 8. Loss of weight, weatherometer WO1. Panel size 7.5 x 23cm

- Alkyd and acrylic latex paints give the highest loss of weight. Polyurethane and fluoropolymer had no weight-loss, except in the WO6 cycle.
- The epoxy paint had a significantly low weight loss, although the gloss disappeared quickly.
- The weight loss method seems to be useful for evaluating low gloss paints, such as the latex paint (where measurement of gloss gives no information).
- The correlation with outdoor climate (W1) is not as good as in the case of gloss measurements.
- The method gives smooth continuous curves which indicate the usefulness of the technique. In most cases, the correct ranking was achieved.

SEM photographs

More than 100 SEM photographs were taken at various stages during the exposure. It was found that washing the paints which were chalking changed their appearance considerably (the loosely anchored particles were washed off). It was considered desirable therefore to work with unwashed panels where possible. The WO cycle photographs were taken after 100 hours and up to 1 400 hours' exposure. A summary of the results is given below.

Alkyd (A)

After 3 to 4 months out of doors, typical chalking could be noted. In the weatherometer, surface defects could be observed after 280h and after 1 300h the paint film was completely eroded (Fig. 9).

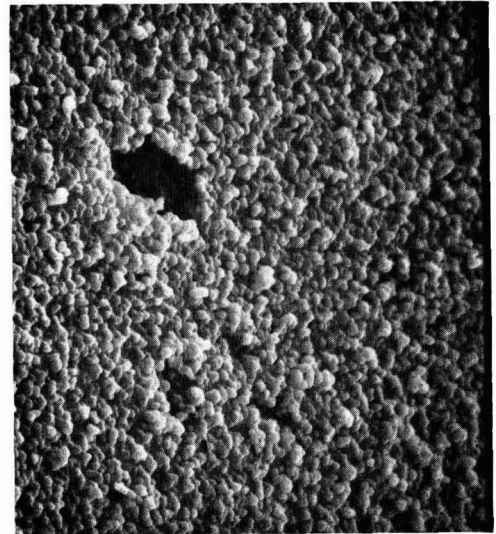


Fig. 9. SEM photograph of alkyd paint exposed for 1 300 hours in WO1. Gloss 20 units. Magnification x 7 000

Chlorinated rubber (C)

Outdoor deterioration could clearly be seen after 12 months in Florida (W3) and approximately 24 months at W1 and W2. The resistances to the cycles were good for up to 1 300 hours.

Epoxy (E)

The film degradation started after 3 months out of doors and 100 hours in WO meters. After 700 hours in the weatherometer

- The WO6 cycle does not differ very much from the other cycles in the case of its results for gloss.

the erosion was complete (Fig. 10). The particles were easily washed off.

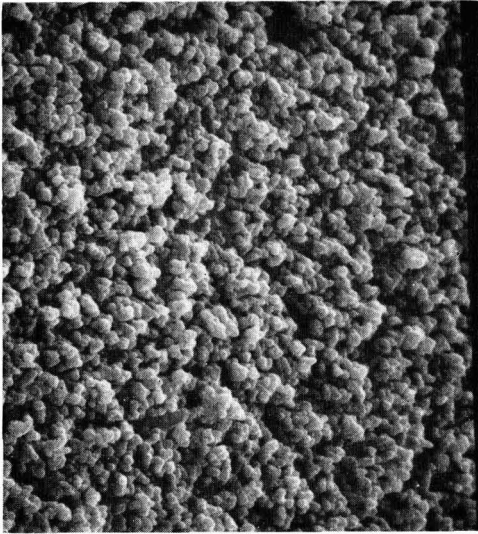


Fig. 10. SEM photograph of epoxy paint exposed for 700 hours in WO1. Gloss 9 units. Magnification $\times 7\,000$

Fluoropolymer (F)

This paint changed very little during WO exposure. A certain amount of degradation could be observed after 21 months in Florida (Fig. 11) as small holes in the paint film. The degradation started at small defects, visible on the unexposed film. These defects are due to imperfect film formation—that is, sintering (agglomeration) of the polymer particles in the fluoropolymer organosol.

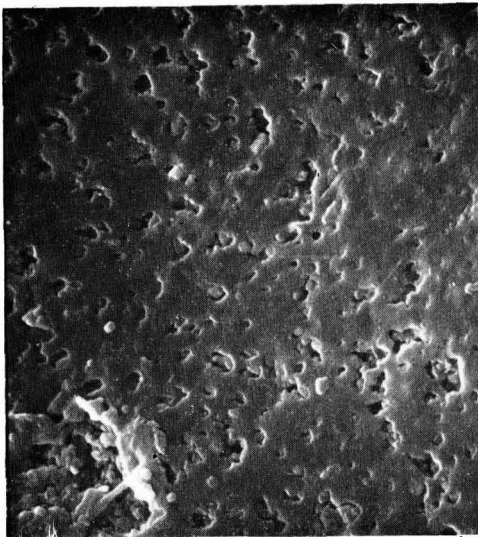


Fig. 11. SEM photograph of fluoropolymer paint exposed for 21 months in Florida. Gloss 22 units. Magnification $\times 7\,000$

Acrylic latex (L)

The layer of binder covering the pigments and fillers in unexposed films disappeared very early during exposure and the underlying inorganic particles could be seen (Fig. 12).

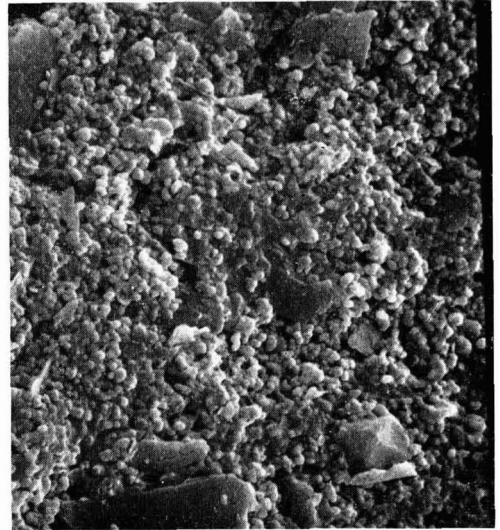


Fig. 12. SEM photograph of acrylic latex paint exposed for 6 months in Florida. Gloss 3 units. Magnification $\times 7\,000$

Aliphatic polyurethane (U)

Very little change was shown after 1 300 hours in WO1 (Fig. 13) but a rather high degree of deterioration was found after 21 months in Florida (Fig. 14). This type of degradation is quite different from the alkyd and epoxy degradations. Areas of binders are left between rather deep craters or erosion spots.

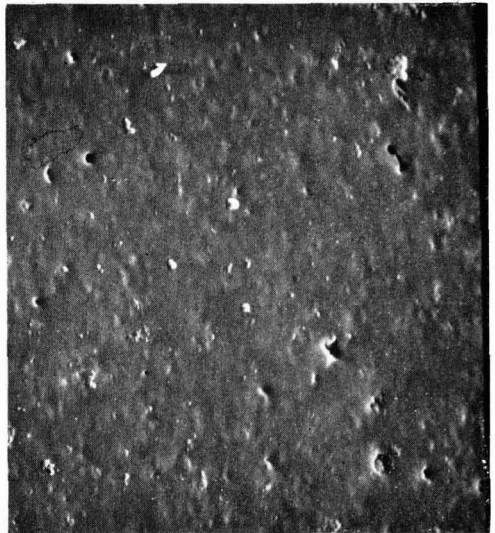


Fig. 13. SEM photograph of aliphatic polyurethane paint exposed for 1 300 hours in WO1. Gloss 88 units. Magnification $\times 7\,000$

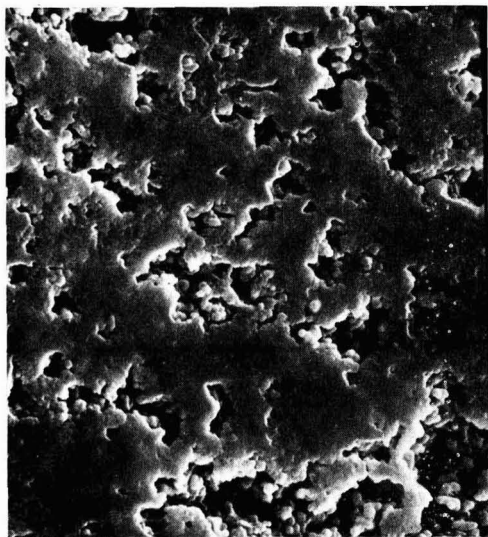


Fig. 14. SEM photograph of aliphatic polyurethane paint exposed for 21 months in Florida. Gloss 40 units. Magnification $\times 7\ 000$

No real analysis is given here concerning the similarity between the morphological deterioration outdoors compared to that due to the WO cycles. In some cases, a rather good correlation was obtained, but there were also some negative results. The influence of rain, snow and wind erosion during outdoor exposure may destroy the "genuine" paint film structure of degradation, especially for paints with heavy chalking.

From the SEM photographs it can be seen that the breakdown is very dissimilar for the different paints. In some cases the pigments are exposed as separate particles (for example, for the alkyd and epoxy paints) but in other cases cracks, holes and "islands" of paint are formed (for example, for acrylic latex and polyurethane paints). Thus, it is difficult to apply the theoretical model described earlier for loss of gloss, where the deterioration is assumed to develop continuously down through the bulk of the film.

Mechanical properties

Microindentation (hardness), tensile strength and elongation at break was studied, the two last properties by using free films.

The micro-hardness increased for all paints. The largest increase was found for the epoxy, chlorinated rubber and acrylic latex paints. A relatively good correlation was obtained between different exposure cycles (outdoor measurements have not yet been completed):

Microindentation hardness correlation			
	WO3	WO5	WO6
WO2	3	3	3
WO3	—	3	3
WO5	—	—	3

The method seems to be promising, but problems may arise with measurements on very coarse pigmented paints and when weathering has exposed much of the inorganic material (see, for example, Fig. 12). To illustrate the types of curves

obtained in this investigation, the results from WO2 are shown (Fig. 15).

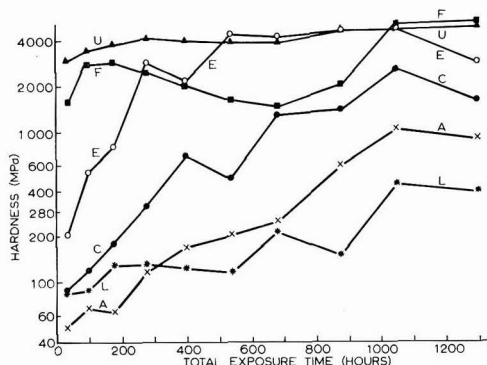


Fig. 15. Micro-hardness. Weatherometer WO2. Expressed as $E/(1-\nu^2)$

For three of the WO cycles (WO1-3), tensile strength and elongation were measured. The fluoropolymer paint was not included in this investigation (no free films could be obtained). The changes in tensile strength and elongation for each paint in the three WO cycles did not differ much, so the results could be used as mean values. It was found that the tensile strength does not change very much during the exposure (Fig. 16), with the exception of the epoxy which shows a decrease. On the other hand, the elongation at break decreases very rapidly (Fig. 17), especially at the beginning of the exposure period. After approximately 400h exposure it was no longer possible to obtain free films of the chlorinated rubber paint. The latex paint and the polyurethane reveal completely reversed mechanical properties. The elongation for the polyurethane and epoxy was so small that it could hardly be measured by the Instron instrument. From this part of the investigation it could be concluded that:

1. Some mechanical properties are changed rather drastically during exposure, especially the elongation at break.
2. Microindentation hardness is a relatively sensitive and easy way of studying the changes in the surface of paint films, but the results do not give complete information about changes in the bulk of the paint film.
3. Measuring the tensile strength and the elongation gives good information about the rheological character of the film. The measurements are somewhat complex (preparation of homogenous free films) and the spread in the results is relatively high.

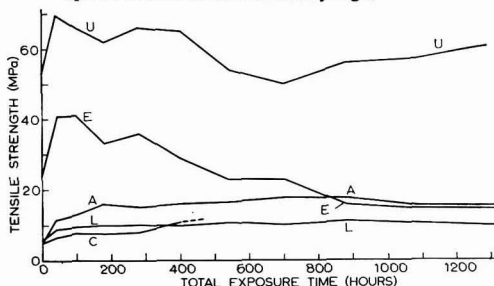


Fig. 16. Tensile strength; mean values from three WO cycles

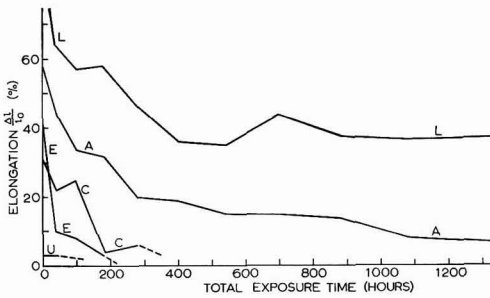


Fig. 17. Elongation at break; mean values from WO cycles

Conclusions

The original properties and general performance of paint films should ideally remain as constant as possible during period of exposure to weathering. As far as the individual properties investigated are concerned, the following conclusions could be drawn:

Measurement of gloss is a very complex and not especially useful method for determining paint film deterioration. Gloss measurements should be supplemented with measurements of loss of weight, especially when paints with low gloss are studied. The scanning electron microscope technique gives good information about the type of paint film degradation. The SEM technique shows that the mechanism of loss of gloss can hardly be described by any simple theoretical model,

Part 2. Painting on plastic materials

Theories and literature

An important reason for this project was to study the adaptability and usefulness of some existing theories about certain relationships between adhesion to a plastic substrate and the surface tension of the two adhering materials. The surface tension of solids is defined by Young's equation based on an equilibrium of forces at the fluid/solid point of contact:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \dots \dots \dots (5)$$

γ_S = surface tension of substrate (solid)

γ_L = surface tension of liquid

γ_{SL} = interfacial tension (solid/liquid)

θ = contact angle

In equation (5) γ_L and θ are easy to measure with suitable apparatus, but γ_S and γ_{SL} cannot be measured directly. By the use of certain theories described below, it is possible to calculate γ_S values based on experimental determination of the contact angles. When a wet paint film with a certain γ_L dries, the surface tension changes and reaches a final value for the dry film γ_S which may differ considerably from γ_L .

Theory I

Refs. 20-22

At the German "Institut für Physik und Chemie der Grenzflächen der Fraunhofer Gesellschaft", Stuttgart, an empirical function of interaction parameters (grenzflächenenergetische Zustandgleichung) has been worked out by Driedgen, Neumann and Sell²⁰ and takes the form:

because the type of degradation is very dissimilar for different types of paints. Considerable changes occur in some mechanical properties of paint films, such as elongation at break and hardness. Thus, a knowledge of changes in these mechanical properties must be considered very important when formulating lacquers and paints.

The question of correlation between outdoor exposures and laboratory testing in weatherometers is very complex and difficult to answer.

The correlation is dependent on the parameters or properties used to express it. One parameter may give good correlation simultaneously with a poor correlation for another. The correlation is also influenced by the type of paint studied. Another problem is to decide the relative importance of the different properties, which may vary with different practical uses.

The exposure results from the different WO cycles did not show large differences, except with the unfiltered carbon arc. If filtered light (borosilicate) is used, the choice of cycle is not very critical.

When gloss was being evaluated, approximately the same deterioration was obtained for the three xenon cycles, whilst greater variations were found for the three carbon arc cycles. The WO cycle with carbon arc and Corex D filter consisting of 1h water without light/2h light/2h water without light/6h light, was found to give the best overall correlation with outdoor exposure, but the difference between this and, for example, the xenon arc exposure cycles is very small.

$$\gamma_{SL} = \frac{(\sqrt{\gamma_S} - \sqrt{\gamma_L})^2}{1 - 0.015 \sqrt{\gamma_L} \gamma_S} \dots \dots \dots (6)$$

By combining the equations (5) and (6), the following equation is obtained:

$$\cos \theta = \frac{(0.015 \gamma_S - 2) \sqrt{\gamma_L} \gamma_S + \gamma_L}{\gamma_L (0.015 \sqrt{\gamma_L} \gamma_S - 1)} \dots \dots \dots (7)$$

The equation is valid for low energy surfaces, such as plastics. By measuring θ for a liquid with known γ_L , the surface tension of the substrate γ_S can be calculated, and by using different liquids, a mean value of γ_S may be obtained. In the literature, diagrams of γ_S as a function of θ for different suitable liquids (which must not chemically attack the substrate) are to be found²¹. See also Fig. 18.

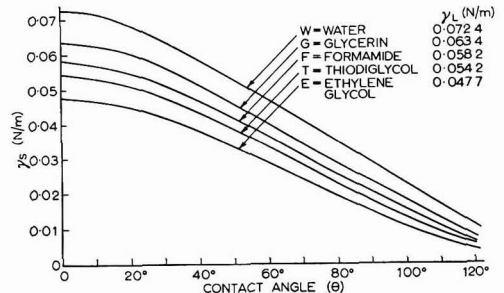


Fig. 18. Diagram showing the relationship between the surface tension of a substrate γ_S as function of the contact angle determined for different liquids

According to a theory described by, among others, Dyckerhoff and Sell²², the adhesion has a maximum value when the surface tension of the dry adhesive or paint film γ_1 is equal to that of the substrate γ_2 , that is, when the interfacial tension between the dry paint film and the substrate is a minimum ($\gamma_{1,2} \approx 0$).

For good adhesion: γ_1 , dry paint film $\approx \gamma_2$, substrate or $\gamma_{1,2} \approx 0$. The principle is illustrated by some results published by Dyckerhoff and Sell (Table 2).

one polar and one non-polar component, better conditions for correlation or prediction of good adhesion should exist.

Experimental results

Ref. 26

To investigate the two theories described above, 12 paints and lacquers were prepared at the Institute, and their adhesion to six different plastic substrates determined by the pull-off

Table 2
Relation between adhesion and surface tension of dry polymer film (γ_2) and plastics (γ) (from ref. 22)

Plastic	γ_1 Plastic N/m $\times 10^3$	Vinyl lacquer $\gamma_2 = 0.03$ N/m		Polyurethane lacquer $\gamma_2 = 0.038$ N/m	
		$\gamma_{1,2}$ N/m $\times 10^3$	Adhesion (MPa)	$\gamma_{1,2}$ N/m $\times 10^3$	Adhesion (MPa)
PTFE	19	1.95	0.1	5.46	0
PP	26.5	0.19	0.1	1.97	0
PE	28.2	0.05	1.5 \pm 0.3	1.43	0
PVCl	33.5	0.18	7.7 \pm 0.9	0.30	5.5 \pm 0.4
PMMA	39	1.21	5.1 \pm 0.4	0.01	8.5 \pm 0.5
PA 6	42	2.15	0.6 \pm 0.2	0.25	3.7 \pm 0.3

Theory II

Refs. 23-25

According to Wu²³ the surface tension of a liquid can be split up into a polar part γ^p and a non-polar part γ^d :

$$\gamma = \gamma^p + \gamma^d \dots \dots \dots (8)$$

For the interaction between a liquid (γ_L) and a substrate (γ_S), Wu deduced the following relation:

$$\gamma_{SL} = \gamma_S + \gamma_L - \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} - \frac{4\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} \dots \dots \dots (9)$$

and by use of Young's equation this gives:

$$\gamma_L (1 + \cos \theta) = \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} + \frac{4\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} \dots \dots \dots (10)$$

By measuring the contact angle for two liquids with known γ_L , γ_L^p and γ_L^d against a substrate, its γ_S^p and γ_S^d can be calculated and thus also the $\gamma_S = (\gamma_S^p + \gamma_S^d)$ for the substrate.

In the work carried out by Toussaint^{24,25} di-iodo methane ($\gamma_L^p = 6.7 \times 10^{-3}$ N/m, $\gamma_L^d = 44.1 \times 10^{-3}$ N/m) and distilled water ($\gamma_L^p = 50.7 \times 10^{-3}$ N/m, $\gamma_L^d = 22.1 \times 10^{-3}$ N/m) were used for measuring the contact angle.

From equation (10) giving γ_S^p and γ_S^d the surface tension of the dry paint film γ_1 , and that of the substrate γ_2 were calculated ($\gamma_S = \gamma_S^p + \gamma_S^d$) and by using equation (9) for the dry paint film/substrate, the interfacial tension between the two materials ($\gamma_{SL} = \gamma_{1,2}$ and L = dry paint film) was calculated.

By using the thermodynamic parameters, "work of adhesion" $W_a = \gamma_s + \gamma_L - \gamma_{SL}$ and "spreading coefficient" $S = \gamma_s - \gamma_L - \gamma_{SL}$, and by postulating that W_a should be large for good adhesion, the conclusion was drawn that the interfacial tension γ_{SL} should be small (approximately zero) and S large (>0) to obtain good adhesion. By dividing γ_S into

method. The plastic materials used were commercial 2-3mm thick panels. The following materials were investigated:

Paints based on:

- 103 Chlorinated rubber ("Pergut S10")
- 104 Physically drying acrylic ("Synthacryl VSC 12/9")
- 105 NC-combination (50% nitrocellulose + "Alftalat AC 436")
- 106 Clear vinyl lacquer ("Vinoflex MP 400")
- 203 Acrylic modified alkyd ("Plexalkyd P 358")
- 204 Air drying tall oil alkyd ("Alftalat AT 576")
- 304 2-component epoxy/amide ("Epikote 1001"/"Versamid 115")
- 305 2-component isocyanate/acrylic ("Desmodur N 75"/"Synthacryl VSC 51")
- 306 2-component water-based epoxy ("Araldite GY 278"/"CIBA X 83/343")
- 307 Clear 2-component polyurethane lacquer ("Desmodur N 75"/"Desmophen 800 + 1200")
- 402 Acrylic latex ("Rhoplex AC-34")
- 404 Acrylic hydrosol ("Elvacite 9011 + 9012")

Plastic substrates

- HDPE = High density polyethylene, black
- PP = Polypropylene, grey
- PS = Polystyrene, black
- PVCl = Polyvinylchloride, red
- ASA = Acrylonitrile/styrene/acrylic ester, grey
- UP = Unsaturated polyester (reinforced with glass fibres), unpigmented

Before applying the paints, the plastic substrates were washed and cleaned with a detergent solution (1 per cent Tween in distilled water). The paints were applied with a doctor blade at a dry film thickness of approximately 60µm. In order to secure a rigid system for the adhesion measurements, the plastic substrates were glued to 19mm thick wallboard panels. Steel "dollies" with an area of 3.14cm² were glued to the painted systems (after 7 days of drying) using a two-component "steel epoxy" as adhesive, and the adhesion was determined with a portable Säberg Adhesion Tester[®].

Experiments based on theory I

The surface tensions of the plastic substrates and the dry paint films were determined by measuring the contact angle for three liquids (water, formamide and ethylene glycol) with a Gardner "Contact angle viewer" and inserting the contact angle values into equation (7). The contact angle values are based on ten observations at different points on the surface and from Fig. 18 a mean of the surface tension γ_s was obtained. These measurements and calculations of γ_s are shown in Table 3. The measured adhesion values and their relation to the surface tension of the adherent materials are given in Table 4. It can be seen that the present investigation has not verified Sell and Dyckerhoff's theory that maximum adhesion should exist when γ_s (paint) $\approx \gamma_s$ (substrate). In many cases, attack by the solvent in the paint on the plastic substrates

Table 3
Surface tension of dry paint films and plastic substrates by use of equation (7) for the three liquids water/ethylene glycol/formamide (W/E/F)

Substrate	Contact angle			γ_s (N/m × 10 ³)			$\gamma_{s,mean}$ (N/m × 10 ³)
	W	E	F	W	E	F	
Paints							
103	84,	69,	74,	33,	25,	29	29
104	82,	58,	58*	34,	30,	37	34
105	74,	48*,	51*	39,	35,	41	38
106	78,	55,	60	36,	31,	36	34
203	92,	84*,	86	27,	18,	22	22
204	91,	64*,	68*	28,	27,	32	29
304	80,	55,	58	35,	31,	37	34
305	80,	53,	60	35,	33,	36	35
306	82,	57,	62	34,	30,	35	33
307	74,	47,	50*	39,	35,	42	39
402	61,	59,	68	46,	30,	32	39
404	64,	—	34	45,	—	49	47
Plastics							
PE	91,	61,	70	28,	29,	31	29
PP	90,	68,	79	29,	25,	26	27
PS	81,	56,	66	34,	31,	33	33
PVCl	82,	56,	60	34,	31,	36	34
ASA	87,	69,	73	31,	25,	29	28
UP	72,	49,	50	40,	34,	32	35

*Slightly attacked by the liquid

Table 4
Relation between γ_s for dry paint films and plastic substrates and their adhesion

Plastics	γ_s (N/m × 10 ³)	Paints												
		203	103	204	306	104	106	304	305	105	307	402	404	
Adhesion (MPa)														
PP	27	< 0.2	< 0.2	< 0.2	—	—	—	0.2	0.3 ± 0.2	—	No wetting	—	—	
ASA	28	3.4 ± 0.1	1.8 ± 0.1	1.3 ± 0.2	—	0.9	1.8 ± 0.3	5.6 ± 0.3	4.8 ± 0.3	6.5 ± 0.3	6.4 ± 0.2	4.3 ± 0.2	3.9 ± 0.2	3.1 ± 0.3
PE	29	0.2	—	—	0.3 ± 0.2	—	—	—	—	—	—	No wetting	—	—
PS	33	3.6 ± 0.1	1.9 ± 0.1	1.1 ± 0.1	—	2.6 ± 0.2	1.1 ± 0.1	—	1.8 ± 0.1	—	—	No wetting	3.0 ± 0.1	5.0 ± 0.3
PVCl	34	3.9 ± 0.3	1.3 ± 0.1	4.0 ± 0.4	0.9 ± 0.2	2.1 ± 0.1	3.6 ± 0.5	1.1 ± 0.1	5.4 ± 0.8	0.5 ± 0.1	—	No wetting	4.8 ± 0.5	4.0 ± 0.4
UP	35	5.5 ± 0.3	1.5 ± 0.1	4.5 ± 0.5	1.3 ± 0.1	2.1 ± 0.2	1.4 ± 0.1	3.6 ± 0.3	5.7 ± 0.3	1.0 ± 0.1	—	No wetting	4.5 ± 0.3	2.5 ± 0.3
		4.1 ± 0.2	1.6 ± 0.1	2.7 ± 0.3	0.8 ± 0.2	2.2 ± 0.2	2.9 ± 0.3	2.4 ± 0.2	4.9 ± 0.3	2.0 ± 0.1	(4.3)	4.0 ± 0.3	3.7 ± 0.3	

— = The adhesion too low to be measured.

could be noticed, which may be one reason for the discrepancy found. Noticeably high adhesion was found for ASA, even though its surface tension was very low (28 × 10⁻³ N/m) and of the same order as for PE, which had very poor adhesion. In one case, namely 105/ASA, the adhesion was so large that the substrate itself broke (cohesion in plastic substrate). If the paints and plastics are ranked according to (overall best) adhesion it is found that:

Again it is difficult to find any reasonable connection between adhesion and γ_s . On the other hand, it is interesting to observe that the four best paints (305, 203, 402 and 404) all contain acrylic binder (in different forms) and that the best plastic is an acrylic polymer.

Obviously, many problems will arise where results obtained under extremely pure conditions—for example, Dyckerhoff

Paint	Adhesion (MPa)	γ_s (N/m × 10 ³)	Plastic	Adhesion (MPa)	γ_s (N/m × 10 ³)
305	4.9	35	ASA	3.7	28
203	4.1	22	UP	3.1	35
402	4.0	39	PVCl	2.9	34
404	3.7	47	PS	2.5	33
106	2.9	34	PP	0.2	27
204	2.7	29	PE	0.2	29
304	2.4	34			
104	2.2	34			
105	2.0	38			
103	1.6	29			
306	0.8	33			
307	No wetting				

and Sell used a microtome to get fresh plastic surfaces—are translated to more practical conditions. The surface tension of a substrate is very sensitive to influences from its surroundings, and it may then be incorrect to use data from the literature for the surface tension for a practical application.

Experiments based on theory II

The polar γ_S^p and non-polar γ_S^d components of the surface tension γ_S of each plastic substrate and dry paint film were determined by measuring the contact angles against distilled water and di-iodo methane and inserting the values found in to equation (10). The calculated values are listed in Table 5.

Table 5

Surface tension γ_S of dry paint films and plastic substrates split up into components γ_S^p and γ_S^d by use of equation (10) for water and di-iodo methane

Substrate	Contact angle		γ_S^p	γ_S^d (N/m $\times 10^3$)	γ_S
	H ₂ O	CH ₂ I ₂			
Paint films					
103	84	—*	—	—	—
104	81	—*	—	—	—
105	72	42	14.5	29.2	43.7
106	78	45	11.7	28.8	40.5
203	93	59	6.1	25.2	31.3
204	90	54	6.8	27.1	33.9
304	80	38	9.8	32.6	42.4
305	80	42	10.2	30.7	40.9
306	80	42	8.7	31.4	40.2
307	72	34	13.5	32.6	46.1
402	61	49	22.0	24.9	46.9
404	65	50	19.8	24.8	44.6
Plastics					
PE	91	50	5.8	29.7	35.5
PP	90	50	6.3	29.3	35.6
PS	80	36	9.6	33.5	43.1
PVCl	81	39	9.4	32.3	41.7
ASA	87	53	8.2	26.8	35.0
UP	72	41	14.3	29.6	43.9

*Di-iodo methane attacks the substrate

The surface tensions determined by this method are somewhat higher than those from the first method described (results in Table 4). By use of γ_S^p and γ_S^d for the two adhering materials the interfacial tension γ_{SL} was calculated from equation (9) and thus S could also be obtained. In Table 6,

the two parameters γ_{SL} and S and also the corresponding adhesion value are given for each combination of paint and plastic substrate. From Table 6, the prediction for good adhesion has been tested, namely that γ_{SL} be less than 2.5×10^{-3} N/m and S be greater than 0. The value 2.0 MPa, which is in the middle range of observed adhesion, was chosen as the value representing acceptable adhesion.

In 24 cases out of 54, the theory and the practical adhesion values corresponded. This is no correlation at all because there are only two alternatives and a statistically random distribution would give the same result as in the investigation. Diagrams showing adhesion as function of γ_{SL} and S gave no reasonable relationships. Thus, it must be concluded from these experiments that the theory is of no use. The value of acceptable adhesion can, of course, be discussed as "good adhesion"; values for PE, for example, are much lower than for UP. From the investigation, it has not been possible to give other limits for γ_{SL} and S which might correspond more precisely to good adhesion; poor adhesion was observed, for example; for S varying between -16 and +10 and γ_{SL} varying between 0.1 and 4.

The wetting tension as a criterion

The parameter wetting tension (WT) is defined as the difference between the surface tension of the solid γ_S and the interfacial tension between solid and liquid. By use of Young's equation:

$$WT = \gamma_S - \gamma_{SL} = \gamma_L \cos \theta \dots \dots \dots (11)$$

The wetting tension is not a material constant, but changes due to interaction between the solid material and its surroundings. If the contact angle is 0, the liquid is said just to wet the surface of the solid, and in this particular case ($\cos \theta = 1$) the wetting tension of the solid will be equal to the surface tension of the liquid, that is $WT = \gamma_L$.

The wetting tension of a plastic surface can be determined in accordance with ASTM D 2578-67.

The surface under test is wetted with drops of liquids with a large range of surface tensions (γ_L). Mixtures of formamide and ethyl cellosolve give γ_L from 30×10^{-3} up to 56×10^{-3}

Table 6

Relation between γ_{SL} and S for the interfacial tensions between dry paint film and plastic substrate and the corresponding adhesion values (MPa)

Paint	PE		PP		PS		Plastics		PVCl		ASA		UP	
	S	γ_{SL} Adhesion	S	γ_{SL} Adhesion	S	γ_{SL} Adhesion	S	γ_{SL} Adhesion	S	γ_{SL} Adhesion	S	γ_{SL} Adhesion	S	γ_{SL} Adhesion
105	-11.9	3.7 0	-11.4	3.2 0	-1.9	1.3 —	-6.2	1.2 0.5	-10.5	1.9 6.4	0.2	0 1.0		
106	-7.0	2.0 0	-6.5	1.6 0	2.0	0.6 1.1	0.8	0.5 3.6	6.2	0.7 5.6	3.1	0.3 1.4		
203	3.8	0.4 < 0.2	4.6	0.3 < 0.2	9.9	2.0 3.6	8.8	1.6 3.9	3.3	0.4 3.4	9.0	3.7 5.5		
204	1.4	0.2 0	1.6	0.1 < 0.2	8.1	1.2 1.1	6.9	0.9 4.0	1.0	0.1 1.3	7.2	2.8 4.5		
304	-8.0	1.2 0	-7.7	0.9 < 0.2	0.7	0.1 0	-0.7	< 0.1 1.1	-8.0	0.7 4.8	0.5	1.0 3.6		
305	-6.6	1.2 0	-6.3	1.0 0.3	2.1	< 0.1 1.8	0.7	< 0.1 5.4	-6.4	0.5 6.5	2.3	0.7 5.7		
306	-5.2	0.6 0.3	-4.9	0.5 0	2.9	0.1 0	1.6	< 0.1 0.9	-5.5	0.4 0.9	2.4	1.4 1.3		
307	-13.8	3.2 —	-13.3	2.8 —	-3.7	0.7 —	-5.1	0.7 —	-13.0	1.9 4.3	-2.4	0.2 —		
402	-21.1	9.8 0	-20.2	9.0 0	-9.7	6.0 3.0	-11.0	5.9 4.8	-18.1	6.3 3.9	-4.8	1.9 4.5		
404	-17.0	8.0 0	-16.2	7.3 0	-6.2	4.7 5.0	-7.4	4.6 4.0	-14.3	4.8 3.1	-1.8	1.2 2.5		

N/m. The surface tension of the liquid which just gives a continuous film during 2 seconds (without break into droplets) is called the "wetting tension" of the specimen. The wetting tension was determined for the plastic substrates, and these values were compared with the overall adhesion:

Plastic	Wetting tension N/m $\times 10^3$	Adhesion (MPa)
PE	34	0.2
PP	31	0.2
PS	37	2.5
ASA	37	3.7
PVCI	48	2.9
UP	48	3.1

A definite tendency towards higher adhesion with increased wetting tension is found. The critical value seems to be around 35×10^{-3} N/m and this value agrees well with the ASTM-standard D 2578-67, which states that the wetting tension for PE-foil should be at least 35×10^{-3} N/m to give proper adhesion for printing inks.

The possibility of increasing the wetting tension of PE by different treatments was studied. This experiment indicated the importance of increasing the wetting tension to increase the adhesion.

To examine the influence of the surface tension of liquid paints, this property was determined with a Du Noüy surface tension instrument. The surface tension was found to be approximately the same for all the paints investigated namely $28-30 \times 10^{-3}$ N/m, except for the acrylic latex paint 402 with the value 50×10^{-3} N/m (paint 404 was not measured.) Thus the surface tension of the liquid cannot be a critical parameter for the adhesion results. This is probably due to the fact that the surface tension of the wet paints is much lower than the wetting tension of the plastic substrates, thus complete wetting is established.

Discussion of results

The results mentioned above show a rather pessimistic picture regarding the existing theories. Adhesion is a very complex property and can hardly be evaluated by use of only one or two surface energy parameters. Chemical bonds and attack by solvent must certainly be considered too. One very important drawback to the investigation is that the surface tension of the dry paint film has been determined by contact angle measurements on the top side and not on the surface facing the substrate.

When the adhesion is strong, it is usually impossible to detach the film from the substrate and the surface tension of the underside of the film cannot be determined.

Measurements carried out at the Institute on dry paint films cured against substrates from which it is possible to prepare free films (PE, "Teflon", tin and air) gave variations in the surface tension due to orientations effects ("epitaxy"). Furthermore, the morphological structure of the upper and

lower film surfaces is different, and this effect may also influence the surface tension.

Conclusions

The experiments indicate that, in practical cases, it is difficult to find any positive relationship between the surface tensions of the two adherents (paint film/substrate) and the adhesion between them. The use of the concept "wetting tension" was found to give some information about the possibility of painting plastic substrates.

Paints containing acrylic binders gave, in most cases, better adhesion than other binders. As expected, untreated non-polar plastics (for example, polyethylene, polypropylene and polystyrene) are poor substrates for obtaining good adhesion, whilst, in general, polar plastics (for example, acrylics, polyesters) are good.

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Discussion at Scarborough Conference

DR J. E. O. MAYNE said that the author had stated that the question of correlation between outdoor exposure and laboratory testing in weatherometers was very complex and difficult to answer. He suggested that the reason for this was that in order to develop an accelerated test, it was necessary to establish the major factor controlling breakdown and

then to examine the effect of intensifying this factor.

Unfortunately, the vehicles in use today broke down by more than one mechanism. They might break down by a process of depolymerisation or by free radical oxidation, or by a mixture of both processes. It followed that no single

accelerated test would be adequate. The mechanism of breakdown had to be established and only after this had been done could a suitable weathering cycle be selected.

MR LINDBERG replied that it could be seen from their scanning electron microscope photographs that the predominant mechanism of breakdown was different depending on the type of polymer and other paint ingredients. It was simply not possible to give only one mechanism for breakdown. In the weatherometer tests reported in the paper, the author had only tested for the effects of light and humidity, whereas out of doors there were such parameters as temperature variations, biological degradation, wind and snow erosion, dirt pick up etc.—parameters very difficult to simulate in an artificial weathering machine.

DR G. de W. ANDERSON said that he could confirm this. Delegates might be aware of the work carried out at the Paint Research Station on ion beam etching as a method for removing successive layers of a paint film so that electron microscopy could be used to reveal the state of dispersion of the pigment. There had been some hope initially that this technique could be used as a very rapid means for determining the durability of the paint; indeed, in many cases this seemed very feasible. Difficulties had arisen, however, when they had studied epoxy systems. Whereas, with the other systems tested, the usual period of exposure to the ion beam was about one or two seconds, with the epoxy systems even 20 minutes' exposure was causing no etching effect. This was despite the fact that epoxies were not particularly durable out of doors.

MR A. N. MCKELVIE said that the author had drawn attention in Fig. 17 to the rapid change in elongation at break for all the films tested and especially the chlorinated rubber, epoxy/amide and polyurethane types. This was probably not unconnected with very small amounts of solvent retention and perhaps too little attention had been paid to the effects of small amounts of solvent retention on durability characteristics. Undoubtedly, retention of elasticity was important for long-life coatings and formulators had tended to overlook the effects of solvent retention in their desire to formulate air-drying and chemically curing systems free from residual tack in the very early life of the film, and had unwittingly developed materials which became brittle and inextensible after a few weeks or months of normal exposure.

MR LINDBERG agreed with Mr. McKelvie, but added that there were other factors, such as micro-cracks in the cured film, which could also significantly affect tests to determine elongation and elasticity.

MR E. L. FRENCH said that he could confirm Mr McKelvie's point. He had been concerned with testing the elongation and elasticity of epoxy films for outdoor exposure

and the films had shown significant retention of solvating material even after exposure for one week at 70°C. This gave significant scatter to the results, particularly for the determination of Young's modulus.

MR LINDBERG reiterated that their films had been tested after about 1 200 hours in a weathering machine; if the films still contained retained solvent after that period, then this had to be considered a characteristic of the film.

DR ANDERSON commented that it was tempting to choose weight loss as the most useful single parameter for assessing durability. In Figs. 7 and 8, this clearly differentiated the two highly durable polyvinyl flouride and aliphatic polyurethane films, even though weight loss did not take account of solvent retention.

MR P. WHITELEY agreed with Dr Anderson, but considered that extensibility was at least as useful: if a film was too brittle, it would not matter how low its weight loss might be.

The author might have saved much time and trouble by determining extensibility on attached films.

MR LINDBERG answered that, of course, extensibility was a very important factor. There were advantages and disadvantages with any method. By measuring weight loss, it was possible to obtain useful results with relatively inexpensive equipment.

MR G. L. PALMER commented that a necessary experimental problem when determining tensile properties of films was that of preparing the test specimens. When these were cut, there would be a considerable risk of making flaws at the edges of the specimens. These flaws would tend to lead to premature tensile failure and erroneous numerical results. Further, this trouble would increase as the films became more brittle as a result of weathering.

The paper assumed that the paint film had a "clear" surface layer and Mr. Palmer wondered whether the author had any evidence to support this supposition.

MR LINDBERG said that he could only repeat that the tests had been made in accordance with the relevant ASTM method for testing the tensile strength of free films. Mr Palmer would know the work which went into preparing a standard test method, and the author felt it justifiable to believe that a standard method of test would give a reasonable answer when properly carried out.

On the second point, he had merely reported that the "clear layer" theory was one of the current theories; his Institute was not concerned with determining whether the clear layer existed in practice.

The theory and practice of film formation by co-ordination reactions involving aluminium compounds*

By J. H. W. Turner, P. Womersley and W. K. H. Lakin

Manchem Limited, Lower Vickers Street, Manchester M10 7LY

Summary

This paper reports progress to date in the evaluation of some complexes of substituted aluminium alkoxides and polar polymeric compounds, such as alkyds.

The effect of aluminium content on compatibility, stability, drying and durability has been studied by using one alkyd at two levels of acid value.

Keywords

Types and classes of coatings and allied products
alkyd coating

Raw materials: driers
aluminium complex
calcium drier
cobalt drier
lead drier
manganese drier
zirconium drier

Equipment primarily associated with analysis, measurement or testing
colour

It is concluded that suitably modified aluminium alkoxides are efficient non-toxic through-driers, giving improved durability, decreased water absorption, better colour and decreased yellowing. The drying behaviour is consistent with the postulated mechanism for both substitution and co-ordination of the polar groups of the polymer with aluminium.

Properties, characteristics and conditions primarily associated with: materials in general
viscosity

coatings during application
drying rate

dried or cured films
gloss retention
water resistance
yellowing

La théorie et la pratique de la formation de feuillets au cours des réactions de coordination entraînant des composés d'aluminium

Résumé

Cet exposé donne un compte rendu du progrès accompli à l'heure actuelle dans l'appréciation de quelques complexes composés des alkoxydes substitués d'aluminium et des polymères tels que des alkydes.

On a étudié l'influence qu'exerce la teneur en aluminium sur la compatibilité, la stabilité, le séchage et la durabilité, à l'aide d'une résine alkyde à deux indices d'acide.

On conclut que les alkoxydes d'aluminium, pourvu qu'ils soient convenablement modifiés, sont des siccatifs à fond, efficaces et non toxiques qui assurent une durabilité améliorée, une absorption d'eau réduite, une meilleure couleur et une tendance à jaunir diminuée. Les caractéristiques de séchage sont en accord avec le mécanisme proposé pour préciser à la fois la substitution et la coordination des groupements polaires du polymère à l'aluminium.

Die Theorie und Praxis der Filmbildung durch Koordinationsreaktionen, in denen Aluminiumverbindungen vorkommen

Zusammenfassung

Diese Arbeit berichtet über bisherige Fortschritte an substituierten Aluminiumalkoxiden und polaren, polymeren Verbindungen, wie z.B. Alkyden.

Der Einfluss des Aluminiumgehaltes auf Verträglichkeit, Stabilität, Trocknung und Dauerhaftigkeit wurde durch Verwendung eines Alkydes bei zwei Säurezahl-niveaus untersucht.

Es wird der Schluss gezogen, dass entsprechend modifizierte

Aluminiumalkoxide wirksame, ungiftige, die Durchrocknung fördernde Trockenstoffe sind, welche höhere Dauerhaftigkeit, reduzierte Wasserabsorption, bessere Farbe und vermindertes Vergilben mit sich bringen. Dieses Verhalten hinsichtlich Trocknung steht im Einklang mit dem postulierten Mechanismus für sowohl Substitution als auch Koordination der polaren Gruppen des Polymers mit Aluminium.

Introduction

Studies by the authors of the reactions, on the one hand, of aluminium alkoxides and related compounds formed by the substitution of some or all of the alkoxide groups and, on the other hand, of polar polymeric compounds, such as alkyd resins, has led to the development of two new classes of aluminium/resin composites, both of which are useful film formers.

The first class was described by one of the authors (JHWT) at the FATIPEC conference in 1972 and is represented in Fig. 1 as a composite in which each of the available polar groups in the medium is involved with one and only one aluminium alkoxide or substituted alkoxide molecule to form what is in effect a poly(mono-alkyd) aluminium alkoxo acid.

The second class was described by the same author at the 52nd Annual Meeting of the Federation of Societies for

*Paper presented at the Association's Biennial Conference held at the Grand Hotel, Scarborough, Yorks, England, from 17 to 21 June 1975.

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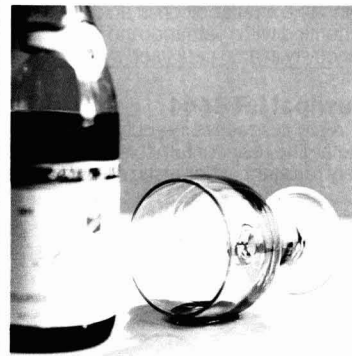
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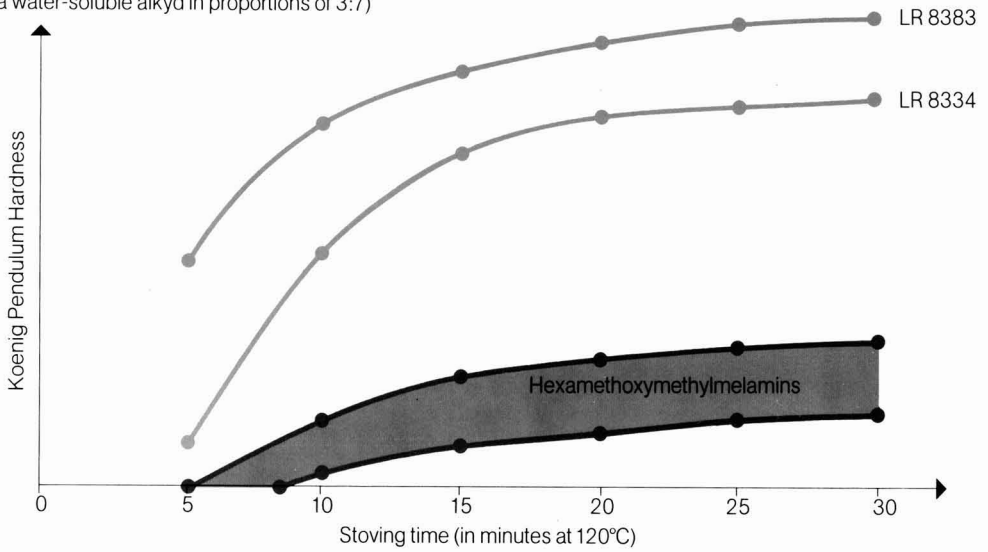
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	low	medium	high	Iso-butanol	Methanol	< 1:1.5	1:3	> 1:5			
Luwipal LR 8334 hw			●		●	●			Isobutanol/ Isopropanol	68%	80-120 (6)
Luwipal LR 8383 hw			●		●	●			Water	70%	80-100
Luwipal LR 8429 h			●	●		●			Isobutanol	54%	250-350
Luwipal LR 8415 hw	●		● SH*		●	●			—	> 95%	ca. 7000 m Pas
Luwipal LR 8444 h			● SH*	●					—	> 95%	~1000

*SH=Acid curing

Characteristics of the New Luwipal Grades

	Reactivity			Etherified with		Compatibility with white spirit			Solvent	Non-volatiles	Viscosity
	low	medium	high	Methanol	Iso-butanol	< 1:1,5	1:3	> 1:5			
Luwipal 010			●	●		●			Butanol/ Xylene	54-57%	450-550
Luwipal 011			●		●		●		Isobutanol	54-57%	360-440
Luwipal 012			●	●			●		Butanol/ Xylene	56-60%	170-210
Luwipal 013			●	●				●	Butanol	51-54%	80-110
Luwipal 030		●		●			●		Butanol/ Xylene	54-57%	60-80
Luwipal 031		●			●			●	Isobutanol	54-57%	180-220
Luwipal 068	●				●	●			—	> 80%	330-370

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Paint (now Coatings) Technology, and is represented in Fig. 2 as a composite in which only the carboxyl groups in the medium is involved with one of the alkoxide groups in the aluminium alkoxo acid formed when an aluminium alkoxide is reacted with an excess of polar diluent. This excess of polar diluent suppresses the substitution reactions which would otherwise occur with the less reactive hydroxyl groups and cause crosslinking and result in thickening on storage.

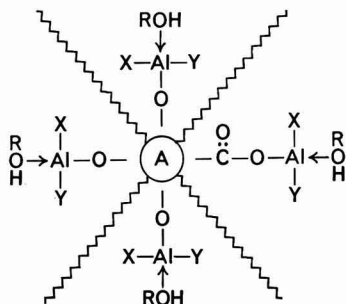


Fig. 1. Postulated structure in which each available polar group in the medium is involved with only one alkoxide molecule

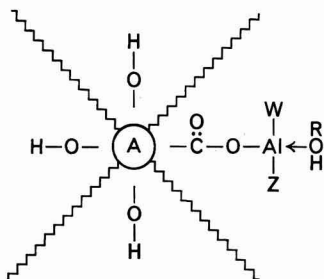


Fig. 2. Postulated structure where an aluminium alkoxo acid molecule forms in the presence of excess polar diluent, and one alkoxide group from this reacts with one carboxyl group in the medium

This paper gives details of the work carried out during the development of the second class of compounds, considers the practical results and relates them to the theoretical predictions.

Alkyd/aluminium composites: General considerations

The reaction which occurs between an alkyd and an aluminium complex may involve some or all of the groups in the alkyd which are capable of adding to the alkoxide or of displacing radicals already associated with the aluminium atom. The energy of association between the aluminium and the different radicals is indicated by the heat of the reaction producing the compound. The carboxyl groups are amongst the most reactive, hydroperoxides and methylene groups activated by ethylenic conjugation are of intermediate reactivity, and hydroxyl groups the least reactive. The complexity of the reaction will depend not only on the different levels of reactivity of the groups, but also on the functionality or number of reactive groups per mole. This will vary with the composition of the alkyd, the process by which it is made, the extent to which it is diluted and the nature of the solvent used. Another

factor will be the type of polar diluent used to suppress the reaction between the aluminium compound and the groups (other than carboxyl) of the alkyd.

The properties conferred by aluminium compounds upon a number of proprietary alkyds of varying composition has been determined. This paper concentrates on one of these alkyds and considers how the properties of the composite formed by association of the alkyd with aluminium compounds are related to the properties of the alkyd itself. The alkyd concerned has the following typical properties:

Type	Soya/penta/ <i>o</i> -phthalic alkyd in white spirit
Non-volatile	70%
Acid value	8.1 mg KOH/g
Hydroxyl value	35.5 mg KOH/g
Viscosity at 25°C	3.5 N s m ⁻² (35 poise) as supplied 0.2 N s m ⁻² (2 poise) at 55% solids
White spirit tolerance	Complete
Phthalic anhydride content	21.5%
Fatty acid content	62%

Experimental

The assessment took into account the following performance criteria:

- Compatibility
- Stability
- Drying performance
- Water resistance
- Durability
- Colour

The tests used for the assessment are described below:

Compatibility

Visual examination of clarity and rheological properties of mixtures was made within 3 hours of mixing. It should be noted that in some cases there was an initial appearance of incompatibility between the aluminium compound and the alkyd solution, which disappears on stirring and on standing. This is attributable to the effect of reaction between the two components.

Stability

The alkyd is diluted to the required solids content with white spirit and the aluminium compound added with gentle stirring at room temperature. The aluminium content is reported as a percentage of resin solids; the solids content of the aluminium alkyd composite solution will be less than that of the alkyd solution because of the solvent content of the aluminium compound.

Gelation is reported, if present 24 hours after mixing, and the viscosity of liquid composites is measured 7 days after mixing.

Drying performance

This was measured on a BK recorder at film thickness $76\mu\text{m}$, temperature 20°C , relative humidity (RH) 67 per cent. The results given here are the arithmetic mean of triplicate determinations of unpigmented films at 50 per cent solids, laid down by a BK applicator.

Water resistance

A $76\mu\text{m}$ thick film of the alkyd at 50 per cent was applied by means of a BK applicator on to a clean and accurately weighed microscope slide. The coated slides were allowed to dry under ambient conditions for seven days and weighed. The slides were then immersed in distilled water kept at room temperature. After the appropriate intervals, the slides were removed from water, blotted to remove water and reweighed as quickly as possible. The results are reported as per cent water increase in film weight, given by:

$$100(C-B)/(B-A)$$

A = weight of the slide

B = weight of film and slide before immersion period

C = weight of film and slide after immersion period

Durability

The paints were pigmented at a 0.8:1 ratio by weight of pigment to alkyd solids, and were made to the following formulation:

Alkyd at 70% solids	100
Titanium dioxide	56
Driers and white spirit	28
	184

The paints were applied in single coats to stainless steel panels at an average dry film thickness of 33 microns. The panels were allowed to age for 14 days at 25°C and 60 per cent RH before exposure to artificial weathering.

The artificial weathering was according to BS 3900 Part F3 with assessments after 250, 500, 750, 1 000, 1 500 and 2 000 hours for:

- (i) Gloss retention— 60° gloss measurements to ASTM D 523
- (ii) Weight loss
- (iii) Chalking to DIN 53-159

Colour

Daylight exposure for 1 500 hours was followed by assessments for the degree of yellowing by:

- (i) "Colormaster" spectrophotometer measurements using the blue filter
- (ii) Visual assessment

Results

Compatibility

Within the limits of 70 to 40 per cent alkyd solids and 0.5 to 4.0 per cent aluminium, compatibility was satisfactory with the exception of some systems, which gelled on mixing.

Stability

Table 1
Viscosity solids relationship at 2% aluminium on alkyd spirit

	Resin solids (%). Diluent: white spirit				
	70	60	50	40	30
Alkyd viscosity (N s m^{-2})	3.5	0.6	0.125	<0.05	<0.05
Composite viscosity (N s m^{-2})	Gel	Gel	Soft gel	0.075	<0.05

Addition of aluminium compound sufficient to provide at least one aluminium atom per carboxyl group (in this case, $8.1 \times 27/560 = 0.39$ per cent Al), should be sufficient, theoretically, to prevent crosslinking by multiple substitution of the labile groups on the aluminium with polar groups in the alkyd. In practice, Table 1 shows that this is not the case, even when the content of aluminium is as high as 2 per cent. The explanation may be found in the high level of association through secondary forces, which is known to be characteristic of alkyd solutions in solvents of low polarity. Such association would increase the effective functionality of the alkyd molecule in its reaction through carboxyl groups with the aluminium compound. The improved stability of more dilute solutions supports this theory. Support of a more practical value comes from the treatment of the alkyd resin with glycidyl versatate (Cardura E, Shell Chemicals Limited) to reduce its acid value. By heating the alkyd with 7 per cent of the glycidyl ester, the properties of the solution were modified as follows:

Viscosity at 25°C	1.5 N s m^{-2}
Acid value	1.2 mg KOH/g
Hydroxyl value	49.2 mg KOH/g

The "alkyd treated" had the stability characteristics given in Table 2.

Table 2
Viscosity solids relationship at 2% aluminium on alkyd solids

	Resin solids (%). Diluent: white spirit			
	70	60	50	40
Alkyd viscosity (N s m^{-2})	1.5	0.325	<0.05	<0.05
Composite viscosity (N s m^{-2})	Gel	0.6	0.35	<0.05

Storage tests now in progress indicate that six months after pigmentation, paints based on the treated alkyd of low acid value showed no signs of instability. When the untreated alkyd is pigmented, stability on storage is less predictable and is dependent on the concentration of the alkyd, the polarity of the diluent, the type of pigments used and the method of pigmentation.

Drying

Table 3
Details of drying*

Metal (% based on alkyd solids)			BK stages (hours)			
Zr	Ca	Al	1	2	3	4
0.09	0.15	—	0.5	1.6	2.4	6.0
—	—	0.5	0.6	5.7	12.1	14.9
—	—	1.0	0.5	1.25	2.3	3.8
0.09	0.15	—	0.5	1.5	2.5	4.0
—	—	0.5	0.5	1.1	1.7	2.6
—	—	1.0	0.5	1.1	1.9	2.4

*All systems contain 0.06% cobalt as metal on alkyd solids.

Water resistance of unpigmented "treated" alkyd composite films

Table 4
Water resistance

Metal (% based on resin solids)				Drying time (hours)	Increase in film weight (%)		
Pb	Zr	Ca	Al		Immersion time (days)		
					3	7	11
0.6	—	0.3	—	5	16.2	33.4†	52.3†
—	0.09	0.15	—	4.5	11.5	122 ‡	133†
—	—	—	4.0	2.5	0.5	10.2	9.9
—	—	—	2.0	3.5	8.2	10.2	9.5
—	—	—	1.0	4.5	5.8	10.1	9.8
—	—	—	0.5	8	5.8	11.3	14.6
—	—	—	0.25	5.5	7.3	15.0	19.6

*All systems contain 0.06% cobalt as metal on alkyd solids

†Films blistering in patches but not detached

‡ Films swollen by blisters and largely detached

Table 6

Weight loss (%) of white paint films after 2 000 hours accelerated weathering

Metal (% based on resin solids)						Pigment	Weight loss (%)
Co	Pb	Zr	Ca	Mn	Al		
0.06	0.6	—	—	—	—	R-CR	10.9
0.06	0.6	—	0.25	—	—	"	10.3
0.06	—	0.09	0.15	—	—	"	9.5
0.06	—	—	—	—	0.5	"	7.4
0.06	—	—	—	—	1.0	"	7.2
0.06	—	—	—	—	2.0	"	9.6
—	—	—	—	0.06	1.0	"	8.1
—	—	—	—	—	2.0	"	10.1
0.06	—	0.09	0.15	—	—	R-CR3	10.8
0.06	—	—	—	—	1.0	"	8.6
0.06	—	0.09	0.15	—	—	K-CR6	12.9
0.06	—	—	—	—	1.0	"	8.1

Durability of pigmented "treated" alkyd composite films

Table 5
Gloss retention for white pigmented films

Metal (% based on resin solids)						Pigment	Gloss levels						
Co	Pb	Zr	Ca	Mn	Al		Exposure time (hours)						
							0	250	500	750	1 000	1 500	2 000*
0.06	0.6	—	—	—	—	R-CR	78	45	38	33	30	30	36
0.06	0.6	—	0.25	—	—	"	62	30	23	19	18	18	27
0.06	—	0.09	0.15	—	—	"	70	37	30	26	24	24	36
0.06	—	—	—	—	0.5	"	88	73	67	66	63	63	58
0.06	—	—	—	—	1.0	"	86	72	68	65	64	59	61
0.06	—	—	—	—	2.0	"	78	58	52	50	48	48	52
—	—	—	—	0.06	1.0	"	90	74	68	66	64	59	63
—	—	—	—	—	2.0	"	82	66	55	56	50	51	54
0.06	—	0.09	0.15	—	—	R-CR3	86	72	66	63	58	57	64
0.06	—	—	—	—	1.0	"	88	80	76	74	71	64	75
0.06	—	0.09	0.15	—	—	R-CR6	83	57	48	42	38	38	55
0.06	—	—	—	—	1.0	"	87	80	78	76	73	72	72

After 2 000 hours, the panels were washed with a detergent solution before the gloss level was measured.

Colour retention of pigmented "treated" alkyd composite films

Table 7
Degree of yellowing of masked portion after 1 500 hours of daylight

Metal (% based on resin solids)						Pigment	Visual rating (0=no change, 5=yellowed)	Colormaster	
Co	Pb	Zr	Ca	Mn	Al			Blue filter	Differential at exposed/masked interface
0.06	0.6	—	—	—	—	R-CR	1	83.5	1.8
0.06	0.6	—	0.25	—	—	"	1	83.1	1.2
0.06	—	0.09	0.15	—	—	"	1	82.8	0.6
0.06	—	—	—	—	0.5	"	1	86.6	1.4
0.06	—	—	—	—	1.0	"	0	87.1	2.0
0.06	—	—	—	—	2.0	"	1	86.7	0.4
—	—	—	—	0.06	1.0	"	1	86.7	0.8
—	—	—	—	—	2.0	"	1	88.1	1.1
0.06	—	0.09	0.15	—	—	R-CR3	2	83.2	0.7
0.06	—	—	—	—	1.0	"	1	85.6	0.6
0.06	—	0.09	0.15	—	—	R-CR6	1	85.0	1.2
0.06	—	—	—	—	1.0	"	0	87.8	1.2

Other colours

Tests are in progress and, at present, these results show similar patterns to those presented by the whites.

Chalking

After 1 500 hours' artificial weathering there was no chalking on any panel.

Discussion

The improvements in stability given to the composite by reduction of the acid value confirms the critical character of carboxyl functionality compared with hydroxyl and other groups of relatively low functionality. This will no doubt be an important consideration in the formulation of polyesters of all types, which are designed to benefit from combination with aluminium compounds.

The drying of the composite appears to involve the accepted stages of oxidative drying with the following additional effects associated specifically with the aluminium component.

- (a) Evaporation of the labile stabiliser
- (b) Substitution reaction between the lower functionality polar groups of the alkyd and the labile alkoxide groups of the composite
- (c) Substitution of the labile alkoxide groups of the composite by water from the atmosphere or the substrate
- (d) Micelle growth through co-ordination bonding of hydroxyl groups generated at stage (c)

Films of the composites had better resistance to water than the alkyd media containing conventional driers. The conventional process of drying by catalysed oxidative polymerisation gives rise to oxidation products which are water sensitive. Aluminium driers, on the other hand, are inactive catalytically, but are able to combine with the oxidation products to form compounds of relatively good water resistance. In addition, because of the nature of the co-ordination bond, when the hydroxyl groups of the alkyd are co-ordinated with or covalently bonded to aluminium they will lose some of their hydrophilic characteristics.

The accelerated weathering results show dramatic improvements in gloss when aluminium replaces the conventional drier systems. There would appear to be an optimum amount of aluminium to give the best gloss, and work reported elsewhere suggests that the optimum amount may be related to the oil length and/or hydroxyl value of the alkyd.

Substitution of cobalt by manganese does not have a significant effect on gloss and yet gives a better white film than does a conventional drier system.

The evidence available regarding the effect of different grades of titanium dioxide, though not conclusive, is in line with what would be expected from the manufacturer's literature.

Conclusions

The object of this paper has been to relate the results obtained from the use of aluminium compounds as paint driers with theoretical predictions of their behaviour. In the experimental

work, technical products of uncertain composition were involved in a number of concurrent and consecutive reactions, and any conclusions drawn must be subject to considerable qualification because of this. Nevertheless, it is considered that the following conclusions provide a significant measure of support for the predictions made.

Paint media of satisfactory stability can be obtained by using aluminium alkoxides, suitably modified with polar diluents, as through-driers for alkyd resin solutions.

Factors shown to enhance stability include low acid value, low viscosity, high aluminium content, solvent polarity and dilution.

Aluminium driers improve the colour, gloss and opacity of many paints by improving pigment wetting and dispersion. There is also evidence of improved mechanical reinforcement and of improved substrate and intercoat adhesion.

The drying behaviour of alkyd media and paints containing aluminium driers is consistent with the postulated substitution and moisture-activated co-ordination mechanism, and is dependent primarily on the availability of reactive groups, such as carboxyls and hydroxyls. Drying rate is generally enhanced by the use of aluminium driers to replace the conventional through-driers, such as mixtures of lead, calcium or zirconium in conjunction with cobalt or manganese surface driers. What is possibly more significant is the relative improvement in film quality resulting from the uniformity of gelation throughout the thickness of the film and the absence of such surface drying faults as wrinkling.

The comparatively low water absorption of immersed alkyd films containing aluminium drier instead of the conventional through-driers is consistent with the postulated theory that hydrophilic polar groups are eliminated by reaction with the aluminium drier.

The improvement in durability is in accordance with the prediction that improved dimensional stability, resulting from a reduction in water absorption, would reduce the rate of film deterioration. In addition, the superior gloss and resistance to chalking of the alkyd with the aluminium drier reflects the lower level of oxidative degradation of a coating containing less oxidation catalyst.

It was expected by similar reasoning that substitution of the lead and calcium driers by the colourless, catalytically inert aluminium would result in improved colour and diminished yellowing and this too was confirmed in practice.

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Discussion at Scarborough Conference

MR G. H. HUTCHINSON drew attention to the studies on the stability of alkyd/aluminium combinations and asked whether the authors had looked at the possible qualitative effects of the carboxylic alkyd species in alkoxide substitution reactions as well as the quantitative effects. For example, in a long-oil *orthophthalic* alkyd, it might be expected that some very low molecular weight species containing carboxyl

groups, as well as high molecular weight carboxylic species, might be present. Mr Hutchinson wondered what effect their substitution might have on viscosity or indeed on subsequent dispersion stability.

In this context, he asked whether the authors had looked at long-oil *isophthalic* alkyds in comparison with their

o-phthalic counterparts. There was the possibility of comparatively less heterogeneity in the *isophthalic* types, which might be in the direction of better pigment dispersion stability over a wider range of aluminium containing composites.

MR TURNER replied that they had looked at alkyds of longer oil length, less highly polymerised and less highly polycondensed, and this was the area in which alkyds of fairly conventional formulation would be found. In particular, for example, a 75 per cent linseed-modified glycerol alkyd of exceptionally low viscosity at an acid value of approximately 13 and with a quite high hydroxyl value and highly recommended for pigment wetting and dispersion, gave excellent stability, provided that the aluminium content was high enough to avoid multiple substitution by the carboxyl groups of that alkyd. For an acid value of 10, the theoretical minimum of aluminium necessary to give mono-substitution of the aluminium was 0.5. An acid value of 13 would, therefore, require a minimum of 0.65 per cent aluminium. In practice, to allow for the heterogeneity of the alkyd media, it had been found preferable to allow double the theoretical requirement. Provided, then, there was 1.3 per cent or more aluminium, there would be perfectly satisfactory stability with that type of alkyd. The authors had looked at a number of others of the same type, and there did not appear to be a problem with these also, provided that the polymerisation and polyesterification was kept fairly low. They had, in fact, gone to the extreme of making just pentaerythritol monophthalic mono-linoleate type structures and using these; they were very interesting because it was possible to obtain very low viscosity at very high solids content. These too gave good stability.

It was necessary to discover more about what was functionality and what was association, but it was possible in practice to achieve stability using relatively low viscosity alkyds of fairly high solids content and fairly long oil length.

MR LAKIN added that they had examined one *isophthalic* acid type alkyd and this was of lower functionality (gave greater stability) than the corresponding alkyd of the same oil length based on *orthophthalic* acid. They were encountering so many differences even with *orthophthalic* acid, however, that it would be impossible to say whether the differences observed were attributable to the different molecular structure of the alkyd or a change from *isophthalic* to *orthophthalic* acid.

MR C. ANSTENIUS said that a lot of the groups in the alkyd which were promoting the adhesion were probably blocked by the aluminium compound. He wondered whether the authors had found that this could adversely affect the adhesion of a paint containing aluminium driers, especially on glossy surfaces.

MR TURNER believed that both intercoat adhesion and adhesion to polar substrates was helped by the availability of groups which were formed by association between the substituted alkoxide and the alkyd, and which were capable of further substitution, not only with the hydroxyl group in the alkyd, but also with hydroxyl groups on the pigment surface or on the substrate surface. They had not made a very detailed study of this, but had generally found that adhesion to substrates, such as wood, glass and most metals, was improved and not diminished by this process. It was possible, however, that with some of the formulations which dried very rapidly—for example, some of the type I compositions—that the film through-dried with quite a lot of solvent still retained, and in this case there could be problems of both intercoat adhesion failure and loss of adhesion to the substrate. In summary, they may have lost functionality by reaction between the alkyds and the aluminium compound, but they had gained it by introducing a reactive group in the form of substitutable groups on the aluminium.

DR K. M. OESTERLE asked whether it was possible to regulate step by step the substitution of the functional groups. He understood that the activity of the polyhydroxyl

group was reduced by co-ordination with the aluminium compound, and wondered whether this could be regulated step by step to give a range of different alkyds of varying reactivity.

MR TURNER replied that they had not investigated this point up to the present time, but he thought there were possibilities of carrying out the type of controlled reaction which Dr Oesterle had in mind.

MR A. G. NORTH commented that his company had had experience in the past of the good performance which could be achieved by pre-reacting aluminium compounds with alkyds, and he was confident that it would be possible to design an alkyd resin which maximised the properties which had been described in the paper. A problem which had always been experienced in the past, however, was that of adventitious water, particularly water adsorbed on pigments in the grinding stage; this had always given rise to stability problems in terms of viscosity.

MR TURNER said that there were basically two problems here. In the case of the first type of medium, where all the reactive groups in the alkyd had been condensed monofunctionally by mono-substitution with the aluminium alkoxide, there was certainly a problem of avoiding the possibility of water which was adsorbed on to the pigments setting off a reaction prematurely. They had experienced this. It was, however, quite easy to scavenge the water by using a medium in which there was an excess of alkoxide that could displace the water or free hydroxyl groups on the pigment. When they had used this scavenging technique, there had been no problems of instability.

In the second class, where they were using a lower quantity of aluminium and a stabiliser, they had encountered no problems of instability due to adventitious water on the pigment.

MR LAKIN confirmed that they had encountered problems of instability with the second type of pigmented system which Mr North had mentioned and they had originally concluded that this was due to water. They had subsequently carried out tests by introducing small amounts of water into an unpigmented system, and this did not present any problems of instability. As a result, they were now investigating the possibility that the pigment surface itself was responsible for the instability, in that since an alkyd was a multi-molecular species in most cases, then if there occurred adsorption on to the surface of a low molecular weight fraction, this effectively increased the functionality of the alkyd with regard to the aluminium. The authors were investigating in this area at the present time to see whether they could determine whether it was the water or adsorption of different alkyd species on to the pigment surface which was causing this effect.

MR TURNER added finally that in the case of the PRA tests where the pigments were not pre-dried, the paints had been kept now for about eight months and the stability of the aluminium-dried paints was actually proving better than those incorporating conventional driers, with regard to both skinning and gelation from the surface.

MR G. R. SIDDLE remarked that titanium dioxide pigments for gloss paints generally had small amounts of moisture present—typically 0.2 to 1.0 per cent. At normal relative humidity, such a moisture content was in reasonable equilibrium with the atmosphere; this moisture assisted dispersion in alkyd media. He asked, when they had scavenged this moisture with excess substituted aluminium alkoxides, whether the authors had noted any differences in the dispersion characteristics of the titanium dioxides when incorporated in the modified alkyds used in this work.

MR TURNER answered that in the limited amount of work

which they had done to scavenge free water or free hydroxyl groups absorbed on the pigment surface, they had found very good wetting and dispersion. They had not studied the effect of variations or whether there was a possibility of detracting

from pigment wetting and dispersion through having too little or too much aluminium present; in fact, it would probably require a pigment manufacturer to judge the significance of some of the results which they had obtained.

Appendix

The results of exposure for 3 000 hours were not available at the time of writing the original Conference paper. These have become available and are included in the following tables.

All gloss levels were determined according to ASTM D 523 at 60° and all exposures were in accordance with BS 3900 Part F3.

Table 8
Drier systems

System	Co (%)	Pb (%)	Ca (%)	Zr (%)	Al (%)	
A	0.06	0.6	0.25			Resin untreated
B	0.06	0.6	0.25			Resin treated
C	0.06		0.15	0.09		Resin untreated
D	0.06		0.15	0.09		Resin treated
E	0.06				0.75	Resin treated
F	0.06				1.5	Resin treated

Table 9
Effect of alkyl treatment and drier type. Pigmentation:
Pigment White 6

Exposure, hours:	0	250	500	750	1 000	1 250	1 500	1 750	2 000
Drier system	Gloss levels								
A	84	67	62	60	57	52	45	35	29
B	80	56	48	46	40	32	35	25	22
C	90	72	67	67	64	57	53	50	43
D	88	69	65	64	60	55	52	46	40
E	90	78	75	76	73	68	67	57	52
F	90	79	78	78	74	69	64	50	50

Table 10
Effect of alkyl treatment and drier type. Pigmentation:
Pigment Black 7

Exposure, hours:	0	250	500	750	1 000	1 250	1 500	1 750	2 000
Drier system	Gloss levels								
A	92	87	87	88	88	88	90	90	88
B	93	88	87	88	87	84	86	84	82
C	92	86	86	86	87	83	87	86	84
D	92	87	86	86	86	85	85	80	82
E	92	90	91	92	92	91	88	91	90
F	92	88	90	90	90	90	91	90	89

Table 11
Effect of alkyl treatment and drier type. Pigmentation:
Pigment Green 7, Pigment Yellow 7

Exposure, hours:	0	250	500	750	1 000	1 250	1 500	1 750	2 000
Drier system	Gloss levels								
A	80	66	60	53	53	52	52	52	48
B	70	53	48	41	41	39	39	39	38
C	84	72	68	64	65	63	62	59	62
D	62	46	38	36	38	35	37	38	37
E	76	66	65	63	65	63	60	62	60
F	81	74	72	76	76	75	65	73	69

Table 12
Effect of alkyl treatment and drier type. Pigmentation:
Pigment Red 6, Pigment Yellow 1

Exposure, hours:	0	250	500	750	1 000	1 250	1 500	1 750	2 000
Drier system	Gloss levels								
A	80	62	55	41	52	47	48	48	42
B	75	56	47	42	45	39	40	38	38
C	86	68	62	55	54	51	52	51	48
D	74	53	47	41	41	36	38	39	35
E	89	77	74	71	72	69	70	69	66
F	86	74	72	72	73	71	72	72	68

Table 13
Weight loss during accelerated weathering (Drier systems and titanium dioxide types as in Table 5)

Exposure, hours:	0	500	750	1 000	1 500	2 000	3 000
System	Weight loss (%)						
1	5.67	6.95	7.67	8.71	9.60	10.86	12.90
2	5.44	6.65	7.41	8.37	9.11	10.25	12.07
3	5.47	6.59	7.18	8.01	8.64	9.53	11.63
4	4.28	5.13	5.57	6.13	6.64	7.39	8.86
5	4.30	5.22	5.61	6.14	6.63	7.18	8.46
6	5.93	7.18	7.68	8.40	8.89	9.62	10.76
7	4.82	5.83	6.40	6.93	7.24	8.14	9.42
8	5.89	7.39	8.15	8.86	9.38	10.13	11.78
9	5.86	7.15	7.90	8.65	9.21	10.81	12.56
10	5.20	6.25	6.85	7.30	7.63	8.60	9.79
11	6.57	8.15	9.08	10.13	10.99	12.95	15.00
12	5.22	5.77	6.17	6.63	7.11	8.15	9.71

Practice makes perfect*

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Summary

The coating of steel is considered from the point of view of the protection provided, as applicable to the motor and structural steel industries. Metal treatment and paint application methods are discussed.

The motor industry works to rigid specifications based on experience and careful testing. The paint is applied under factory conditions which are controlled and nearly ideal, with the result that paint performance in practice approximates to what would be expected on theoretical grounds.

Keywords

Types and classes of structures of surfaces to be coated
steel

Supplies and other materials primarily associated with analysis, measurement or testing

exposure panels

The structural steel industry operates at a great disadvantage due to the necessity to transport the factory painted parts to the site of construction, at which they may be stored under adverse conditions for long periods before erection and the application of the final paint system. Due to the environmental conditions during storage and final painting, the practical performance may differ widely from the theoretical behaviour.

Processes and methods primarily associated with surface preparation before coating

grit blasting
surface preparation

Properties, characteristics and conditions primarily associated with the environment

specification

Usage rend maître

Résumé

On considère les revêtements appliqués à l'acier au point de vue de la protection assurée aux automobiles et aux charpentes en acier. On discute les méthodes de prétraitement et d'application de peintures.

L'industrie d'automobiles fait appel aux normes sévères basées sur l'expérience et les systèmes d'essais rigoureux. La peinture est appliquée à l'usine sous des conditions bien contrôlées et quasi-ideales, de sorte que le rendement de la peinture est semblable dans la pratique à celui que l'on s'attendrait aux considérations théoriques.

L'industrie de charpentes en acier s'opère sous de graves inconvénients dus à la nécessité de transporter les éléments peints de l'usine au pied d'oeuvre où ils peuvent être stockés pendant de longues périodes sous des conditions adverses, avant d'être érigés et avant de l'application de la peinture de finition. A la suite des conditions environnementales lors du stockage et de la peinture finale, le rendement dans la pratique peut être largement différent du comportement théorique.

Übung macht perfekt

Zusammenfassung:

Der Anstrich von Stahl wird vom Standpunkt des durch ihn gewährten Schutzes betrachtet, wie solcher für die Automobil- und Konstruktionsindustrien in Frage kommt.

Die Automobilindustrie arbeitet nach auf Erfahrung und sorgfältiger Prüfung aufgebauten strikten Liefervorschriften. Die Lacke werden im Werke unter kontrollierten und beinahe idealen Bedingungen aufgetragen, mit dem Ergebnis, dass ihr Verhalten sich in der Praxis dem nähert, was aus theoretischen Gründen zu erwarten ist.

Die Konstruktionsindustrie arbeitet unter sehr nachteiligen Bedingungen, weil die im Werke vorgestrichenen Teile auf die Konstruktionsbaustelle transportiert werden müssen, wo sie vielleicht unter ungünstigen Bedingungen lange vor dem Einbau und Auftragen des endgültigen Anstrichsystems gelagert werden. Das Verhalten in der Praxis kann von dem theoretischen Verhalten als Folge der in der Umgebung herrschenden Verhältnisse während der Lagerung und der letzten Anstricharbeiten stark abweichen.

Introduction

The estimation of paint film performance is so complex that it can be more of an art than a science. Substrate, environment (both during and after application), method of application, film thickness, ingredients used and method of manufacture of the paint are just some of the factors that can play an important part in the end result, and amongst those mentioned, painting practice has not been included.

In asking whether the reality of paint performance matches the theory, it is important to consider the assumptions on which the theory is based. Many of these assumptions can sometimes be shown to be completely invalid.

In this paper the only substrate to be considered will be steel, and painting practice in the motor industry will be compared and contrasted with that used in the steel construction industry in the painting of steel bridges. In both cases paint is required to fulfil its two normal functions (protection and decoration), but in each there is a special protective function, the prevention of steel corrosion.

The theoretical or expected performance of a paint coating is based on the knowledge of the properties of the constituent polymers and pigments based on tests carried out usually in the laboratory on coatings prepared from those constituents. Variations in composition are made under controlled conditions to obtain optimum properties for the intended end use.

*Paper presented at the Association's Biennial Conference held at the Grand Hotel, Scarborough, Yorks, England, from 17 to 21 June 1975.

If good painting practice is observed and the theory is soundly based, results will closely equal expectations, but failures blamed on bad painting practice or bad paint are often due more to a lack of recognition of service conditions.

The motor industry

Motor manufacturers throughout the world are sophisticated buyers of paint coatings, and their specifications state in detail the properties required and how they are to be assessed. It is significant that whilst the general outlines of composition are given, there is no attempt closely to specify the proportions of the various ingredients or their specific nature.

Specifications

The essential requirements of a specification issued by a major motor manufacturer for the supply of thermosetting acrylic enamel are described below.

The specification is entitled "Acrylic baking enamel, exterior quality", and this is the only limitation on the composition. The potential supplier is required to state normal physical constants, such as volume, and weight solids, and spreading rate. The required opacity and film thickness are stated, and a period of exterior weathering resistance in Florida is required, with permitted gloss levels before and after this period of weathering being stated. Chemical, humidity, and water resistance tests are also specified in detail, as are tests on intercoat adhesion, covering even situations of misuse, such as over-bake, or where "in-line" repairs are necessary. Other tests are included to cover performance under conditions of extreme temperature fluctuation, and to meet other special conditions likely to be found in service. Similar specifications exist for primers, and in all cases the accent is on meaningful performance tests closely related to potential service conditions, rather than attempts closely to specify composition. Quality control and approval tests are carried out on all batches before delivery is accepted.

The substrate

The steel substrate is cold rolled steel sheet free from scale which is automatically cleaned and phosphated before use under strictly controlled conditions, the final rinse being with de-ionised water. Standard panels prepared from the same steel by the same method are used for test purposes in the laboratory. Even so, as a special precaution, when testing for corrosion resistance, rolls of "corrosion prone" steel are selected for this purpose in order to ensure that the worst possible conditions in practice are reproduced.

Painting practice

Painting practice in the motor industry is usually as near perfect as any paint supplier has a right to expect. An even temperature is maintained, and the air supply is often filtered before reaching the spray booth, the work is carefully controlled and inspected at all stages. Defects do arise in the finish, however, due for example to mechanical damage during assembly, and paint repairs are necessary. An example of a fault which can arise is in a new design of car which has certain problems of body assembly, leading to larger than normal amounts of solder in certain areas, and so to a greater tendency for paint defects to occur, hence more cars to repair. The stoving of the repair may then be reduced in order to accelerate throughput and prevent a build up of cars requiring treatment.

Residual solvent left in the film in this situation can cause early blistering of the finish when the cars are driven outside to storage sites on completion.

Testing

In spite of the efforts of both supplier and user to provide comprehensive and meaningful performance test specifications, situations can arise where new tests are required. An example of this arose from the development of metallic finishes with a high degree of transparency. This caused greater emphasis to be placed on the chalk resistance of primer surfacers in order to maintain good intercoat adhesion between primer and finishing coat on weathering.

Conclusion

Because of the trouble taken to perfect all aspects of the painting operation from preparation of the substrate to painting practice and testing, the motor industry achieves in general very good correlation between the theory and the reality of paint performance. The corrosion problems, so often referred to in connection with the motor industry, are matters of economics and design rather than a failure to achieve anticipated paint performance.

The steel construction industry

Refs. 1-2

The protection of large steel structures presents a much more difficult problem in the control of the environment and the general conditions under which painting is carried out. Much of the painting has to be done out of doors. Even in the case of new structures, whilst part of the paint protection system can be applied in the fabricating shop, steelwork must necessarily be taken to the site as sub-assemblies and be erected and welded there before the final protective paint coats are applied, so that even gaining access to the surface to be painted can often be difficult.

McKelvie¹ has shown that suitable outdoor atmospheric conditions for painting as laid down in CP. 2008² exist only, in some areas, for one out of every two normal working days, and even at the height of summer for only three out of every four. Even when temperature and humidity conditions are right, the heavy masses of steelwork used in bridge construction lag behind the atmospheric temperature, and are often cold and damp for up to two hours after weather conditions are deemed satisfactory for general painting.

Specifications

With these and other difficulties in mind, specifications for the painting of structural steel have tended to concentrate more on factors associated with substrate preparation and assembly than on the paint itself. Some specifying authorities believe that composition specifications for the paint used, rather than reliance on proprietary brands, would help to remove some of the uncertainty in paint performance, and the new CP.2008 will undoubtedly contain some recommendations of this type. Unlike the motor industry, the use of performance testing in specifications is almost unheard of, and though the Department of the Environment, British Rail and the Quality Assurance Directorate are doing much to improve the situation, a great amount remains to be done.

The substrate

Refs. 3-6

For the effective paint protection of new steel structures the importance of the removal of mill scale is now well recognised, and grit blasting or pickling is the normal pre-treatment procedure adopted, but despite being clean and free from scale after these treatments, the surface is a long way from the quality of surface achieved in the motor industry.

If the surface is prepared by grit blasting, the surface profile will be rough with sharp peaks, often with as much as 100 μ m from peak to trough. The steel presents a highly reactive surface without the phosphate protection given in the motor industry, and will rust rapidly unless protected by paint within a very short period³. Pickling, though giving less sharp peaks, still leaves deep pits in the surface, although the Duplex process does provide a phosphate pretreatment as some protection before painting.

Painting a grit blasted surface, because of the surface profile, uses approximately 30 per cent more paint than a film of equal thickness on a flat surface⁴. The performance of anti-corrosive primers can vary widely on such a surface according to their tendency to flow away from the peaks. Keane⁵ and many others have shown that paint film thickness is an important factor in the prevention of steel corrosion, yet errors can easily arise in the measurement of film thickness on a grit blasted surface.

Table 1 shows the error that can arise due to variations in the thickness of the base steel. In these experiments a polished steel panel was taken and paint applied, the instrument zeroed on the base steel of 1.4mm thickness and the film thickness measured. This panel was then stacked on to other steel to give increased thickness of steel and the film thickness variations were noted with both Permascope, and Elcometer film thickness gauges. It will be noted that the error at 2.5cm steel thickness is now approximately two per cent lower with the Permascope and four per cent higher with the Elcometer Inspector (Series A). The experiment was repeated (Series B) with a higher film thickness of paint; again the Permascope gave a low reading, this time of approximately eight per cent error, and the Elcometer again a high reading. This error increases as the total paint film thickness increases, and on a normal complete protective system of 250 μ m dry film thickness, therefore, the error could be quite significant.

Table 1

Errors in measuring paint film thickness due to variations in total thickness of substrate

System	Steel thickness (mm)	Paint film thickness average readings (μ m)	
		1. Permascope	2. Elcometer
A	1.4	14.7	13.7
	2.8	14.7	14.2
	5.6	14.7	14.0
	25.0	14.5	14.2
B	1.4	44.2	43.2
	5.6	41.9	45.0
	16.8	40.9	46.0
	28.0	40.9	46.2

Whilst error due to this cause easily can be avoided when inspecting the coating of sheet steel, it is not always so easy when inspecting partly or fully fabricated steelwork.

The next experiment was to examine errors that could arise due to steel profile variations. The instrument was again zeroed on plane steel and then measured after fine, medium and coarse grit blasting on panels of the same total thickness of steel plate 6.3cm (0.25 inch) with the results shown in Table 2. No paint was applied in this case, but it will be seen that between polished steel and coarse grit blasting of approximately 100 μ m peak-to-trough distance, a reading of 21.6 μ m film thickness is obtained, although no paint has actually been applied.

Table 2
Errors in measuring paint film thickness due to substrate surface profile variations

Substrate	Average reading (μ m)	
	Permascope	Elcometer Inspector
(1) Finely grit blasted steel	2.8	2.8
(2) Medium blasted steel at 0.2 MPa (30psi)	19.6	13.7
(3) Coarse blasted steel at 0.4MPa (60psi)	21.6	21.1

Similar experiments were then carried out on multi-coat paint systems on grit blasted steel, this time using very fine grit blasting of type (1) in Table 2, which gave a peak-to-trough profile of average depth around 25 μ m. The paint used in this case was a hard stoved enamel paint system in order to minimise errors arising from paint softens and indentation by the measuring instrument.

Table 3
Thickness of multi-coat systems on fine grit blasted steel

	Average readings (μ m)			
	Permascope		Elcometer Inspector	
	Actual	Corr*	Actual	Corr*
(A) 1 coat on plane polished steel	14.7	14.7	13.7	13.7
(B) 3 coats on plane steel	44.2	44.2	43.2	43.2
(C) 4 coats on plane steel	55.1	55.1	57.7	57.7
(D) 1 coat on fine grit blasted steel	14.2	11.4	14.0	11.2
(E) 3 coats on fine grit blasted steel	42.2	20.6	39.4	18.3
(F) 4 coats on fine grit blasted steel	57.2	35.5	56.6	35.5

*Corr = corrected for zero error

The corrected film thicknesses shown in Table 3 are those where zeroing of the instrument using shims had been carried out immediately adjacent to the point where the reading was taken. The actual film thickness is that recorded when the instrument was zeroed on plane steel of corresponding thickness. Thus with incorrect zeroing, the measured film thickness could be as much as 50 per cent more than that actually present.

It is important, therefore, when measuring paint film thickness on grit blasted steel to adjust the instrument using shims of known thickness over steel of the right thickness blast cleaned to the same profile as the steel to be inspected. Keane and Shoemaker⁶ have dealt with this subject in detail.

Painting practice

Refs. 7, 8

For unavoidable reasons of climate mentioned earlier, site painting is often carried out under poor conditions, and in the steel fabricator's works itself, though many improvements have been made, painting shops are often cold, dirty and badly lit.

Contamination of paint surfaces with blasting grit is a frequent cause of trouble, but when all possible steps are taken to obtain the best possible painting procedures, the tolerance of the paint system to poor drying conditions and resistance to damage during handling of the newly painted steelwork are important factors to be considered in conjunction with the environment when assessing anticipated final performance.

Environmental factors are often grossly misunderstood when designing accelerated test methods for protective paints for structural steel. Junge^{7,8} has shown that the pH of unpolluted rain, due to carbon dioxide, is 5.6. In contrast, the pH of urban rain is 4.5 and often as low as 4.0 due mainly to oxides of sulfur polluting the atmosphere. Experience has shown that this acidity is not such a serious factor where the surfaces are open to sun, rain and wind, but on the downward facing surfaces of large masses of structural steel, the industrial contaminants increase in concentration, the surfaces are not washed by rain, and yet they remain damp for long periods due to condensation. Such surfaces can present extremely severe conditions for paint breakdown and loss of adhesion.

Testing

Refs. 9-12

The performance testing of paints for the steel construction industry lags far behind that of the automotive manufacturing industry.

Boxall and Fraunhofer⁹ list in a paper on anti-corrosive primers, four mechanisms by which paint protects steel from corrosion:

- (a) through the formation of the surface layer on the metal, which is relatively impervious;
- (b) through the leaching of inhibitors from the pigment in the coating;
- (c) cathodic protection of the metal, typically by the inclusion of zinc dust in the paint film;
- (d) through the formation of an inhibitive soap by the hydrolytic decomposition of polymeric fractions within the coating.

Thus protection by physical, chemical and electro-chemical mechanisms work in combination. In spite of this there are often attempts to evaluate paint coats for corrosion protection by electrical methods only. Hearst¹⁰ of the United States Naval Civil Engineering Laboratory and many others carried out such work with little success.

McKelvie¹¹ compared the performance of paints in the commonly accepted accelerated tests, such as salt spray,

SO₂ resistance by Kesternich method, and humidity cabinet, with results from practical tests on the underside of the Tinsley Viaduct, and also at sites at Shoreham and at Teddington. His conclusion was that artificial environmental tests do not correlate very well with site exposures. It was felt, however, that the breakdown of test systems was sufficiently rapid in the practical site exposures to allow conclusions to be drawn from these.

The acceleration factor of so-called "accelerated tests" is not always very great. For example, the author has compared British Standard 3900 Specification Salt Spray Test with exposures at the tidal zone under the Forth Road Bridge. A number of protective systems for zinc based on epoxy and oleoresinous media was evaluated, and the degree of protective breakdown achieved in 12 months at the tidal zone took at least six to nine months to achieve in the salt spray cabinet.

A final important cause or failure in practice is the period of weathering on large structures during the erection period. Part of the paint system is applied at works, and then the steelwork is transported to the site. The period between the application of the works coats and the final painting on site can be prolonged, and 12 to 18 months' exposure with works coats only applied is quite common. During this period, steelwork may be covered in water for long periods, and may be subjected to extensive contamination by pollutants. Deck sections are sometimes stored in the river, and towed out to the bridge site for erection.

The works coats must, therefore, give complete protection in themselves, must be capable of easy cleaning, and also give good adhesion with the site coats to be applied at the completion of the construction work.

An illustration of the problems which may be encountered with polyurethane and epoxy paints in this situation is shown in Tables 4 and 5 below.

The paints in Table 4 were recoated after one month's ageing of the first coat in the laboratory. Duplicates were then stuck together with epoxy cement and pulled apart in a Hounsfield Tensometer. Normal crosshatch and tape adhesion tests were also carried out on the re-coated paints after 80 hours exposure in the humidity cabinet.

In Table 5, the same procedure was used but this time the paints were recoated after the film had been subject to three months' exterior exposure. Surfaces were washed clean of contaminants but not subjected to mechanical abrasion before re-coating. A practical example of a failure arising from this cause was reported by Bishop¹² in a series of trials of experimental paint systems carried out on bridge structures at Loudwater and Baldock. An epoxy isocyanate system showed severe intercoat adhesion failure between works and site applied coats, although adequate steps were taken to remove contaminants from the surface before painting. Laboratory adhesion tests failed to reproduce the failure but exterior exposure before repainting was not included in the series of tests carried out.

Table 4
Results of tests on polyurethane system

Ref No.	Description	Results of direct pull-off tests			Results of crosshatch tests
		Mean joint strength (MPa)	Type of failure		After 80 hrs in the humidity cabinet
1	Matt fully cured polyurethane. 50% MIO† pigmentation using aromatic isocyanate.	23.7	100% cohesive	—	0
2	Matt polyurethane, titanium dioxide pigmentation with amorphous extenders and aliphatic isocyanate.	29.7	100% cohesive	—	0
2a	As 2 but using aromatic isocyanate.	38.2	95% cohesive	5% intercoat adh.	0
h2a	As 2a but undercured, using 50% of theoretical isocyanate content.	30.1	50% cohesive	50% intercoat adh.	0
3	Gloss polyurethane, titanium dioxide pigmented, aliphatic isocyanate.	22.0	—	100% intercoat adh.	10% iaf* (b)**
3a	As 3 but aromatic isocyanate cured.	43.9	100% cohesive	—	0
h3a	As 3a but with 50% reduced isocyanate.	20.0	20% cohesive	80% intercoat adh.	0
4	As 3 castor oil modified.	10.0	—	100% " " "	0
4a	As 3a " " "	29.1	10% cohesive	90% " " "	0
5	As 3a hydrocarbon resin modified.	41.9	50% " "	50% " " "	0
6	As 3a chlorinated rubber modified.	36.2	80% " "	20% " " "	0
7	Alkyd modified polyurethane with additional alkyd.	21.7	—	100% " " "	100% iaf* (b)**
8	Oil modified polyurethane gloss enamel.	20.1	5% " "	95% " " "	100% iaf* (b)**
9	Alkyd modified polyurethane.	43.8	40% " "	60% " " "	0

Reduction in isocyanate does not, therefore, help adhesion—compare 2a and h2a. Aromatic isocyanate was better than aliphatic. Systems 1, 2a, 3a, 5 and 6 were the only ones showing reasonable intercoat adhesion on this test (pull-off).

The cross hatch tests, though not as sensitive as the pull-off tests, do not show any important disagreement. The coatings from this series, giving reasonably good intercoat adhesion at this stage, were then weathered and the tests repeated as shown in Table 5.

* iaf = intercoat adhesion failure
 ** (b) = blistering
 † MIO = Micaceous iron oxide

Table 5
Repeated tests after exterior weathering

Ref. No.	Description	Mean joint strength (MPa)	Type of failure
1		10.5	100% cohesive
2a		14.2	100% intercoat adhesion
3a	Repeat of polyurethanes in Table 4.	10.7	100% " " "
5		8.4	100% " " "
6		11.7	100% " " "

In this case, 100% intercoat adhesion failure occurred in all cases, except 1.

A set of various epoxy formulations were then tested with the results shown below.

10	Aromatic amine cured epoxy.	12.1	100% intercoat adhesion
11	Polyamine cured epoxy.	20.3	60% " " "
12	Polyamide " "	14.9	90% " " "
13	Phenoxy. " "	18.6	— " " "
14	As 10+ 10% phenoxy basin.	12.4	100% " " "
15	As 10+ chlorinated rubber.	13.9	100% " " "
16	Water dispersible polyamide cured epoxy.	16.6	— " " "
17	As 12+ 25% excess polyamide.	13.1	100% " " "
18	As 12+ 10% phenoxy resin.	13.1	100% " " "
19	As 10+ 10% phenolic resin.	7.4	100% " " "
20	As 10 with MIO pigmentation 35% PVC.	7.7	100% " " "
21	As 20 with 48% PVC.	1.5	— " " "
22	As 11 with MIO Pigment 35% P.V.C.	4.1	50% cohesive 50% detachment from substrate

Conclusions

In the painting of steel structures, perfect painting practice is difficult if not impossible to achieve, but a gap between theoretical expectations and practical results can arise due either to selection of unsuitable test methods, to lack of adequate inspection during the progress of the work, or to failure to recognise the essential practical environmental conditions under which the work must be carried out and in which the structure must remain throughout its life.

Acknowledgments

The author wishes to thank the Directors of Inmont Limited for permission to publish this paper.

[Received 11 February 1975]

Discussion at Scarborough Conference

MR F. G. DUNKLEY said that Mr Claxton recognised the gap between theory and performance of paints and suggested that this largely arose from interfacial problems. These were just the areas that painting inspection could do most to influence, or at worst to monitor the conditions which had given rise to the failure.

With regard to the difficulties of measuring dry film thickness, the author was right to draw attention to the possible errors arising from this cause, but it should be pointed out that the sources of error were known and the necessary technique to eliminate these was also known and was in use by responsible inspection organisations.

MR A. N. MCKELVIE added that the low thickness values (Table 3) on blast cleaned panels indicated that the materials tested flowed away from high spots, and for the blast primer a value of 11 microns was being obtained, compared with 14 to 15 on a flat surface. The author seemed to have discovered a good method of test for selecting paints which did not flow away from high spots, and this might provide a useful laboratory sorting test without recourse to site testing.

MR CLAXTON said that comparison of film thicknesses were carried out on commercial grit-blasted steel using the Steirand, Elcometer Inspector, Elcometer Pull-Off Gauge, Permascope and Minitector instruments.

Film thicknesses were measured using a system of one-coat of polyvinyl butyral blast primer and three-coats of zinc phosphate epoxy ester primer, both materials being in regular commercial use and having given every satisfaction for peak coverage and exterior durability over a considerable period. There was, therefore, no possibility that the following discrepancies in results had arisen because material had abnormally sagged away from the peaks of the blast profile. In every case when using the instruments, the manufacturer's instructions had been strictly followed regarding the zeroing of the instrument prior to taking the measurements, and all measurements had been carried out on flat sheets avoiding edge effects.

The Steirand instrument, of course, cut a wedge through the film, which was then examined under a microscope and the film thickness calculated from a knowledge of the angle

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of the wedge and visual measurement of the length of each particular coat in the section.

The other instruments were all magnetic, although the Minitector and Permascope were based on an electro-magnetic system of measurement.

The theoretical dry film thicknesses per coat were obtained by wet film thickness measurement, using the percentage volume solids of the paint.

The Table (below) gave the individual readings so the degree of correlation could be seen, and the theoretical value was averaged over wet film thickness measurements taken on all the separate panels applied.

It could be seen that the Steirand instrument gave for each separate coat and for the total paint system, almost perfect correlation with the theoretical figures, except in the case of the first epoxy ester coat where one reading was rather high. In all other cases the individual coats after the first, read consistently low, the error increasing up to the second epoxy ester primer coat, when it could be presumed that the steel profile was filled. After this period, the error appeared to remain constant with subsequent coats, but did not get any less as the film thickness increased.

If measurements of site painting were carried out, therefore, zeroing the instrument on the painted steel ex-works, it was likely that accurate film thickness would be obtained. The region of error was in the application of the first priming coats before the steel profile was properly filled, but the Steirand measurements showed that it was not wholly explained by sinkage of the paint into the profile of the steel.

All the magnetic film thickness instruments agreed remarkably well except for the Permascope at the second and third priming coat stage, where it was necessary to switch from one scale to another. This involved re-zeroing the instrument and, therefore, introduced other complications.

MR A. B. LOCK said that Mr Sherwood, in his joint paper with Mr McKelvie, had referred to paint problems and failures arising directly from design faults and stressed the need for the industry more actively to advise architects. Mr Lock wondered whether those concerned with large civil engineering projects, such as the design of bridges, were

Comparison of paint thickness gauges—Multicoat system

Method		Blast primer	Blast + 1st primer coats	Blast + 1st + 2nd primer coats	Blast + 1st + 2nd + 3rd primer coats	Thickness (μm)			
Theoretical—per coat:		13 – 20	50 – 60	50 – 60	50 – 60				
Theoretical—average totals:		17	72	127	182				
Steirand: (Optical)	(a)	20	78	125	185				
	(b)	20	90	125	185				
	(c)	25	78	125	185				
Elco Inspector: (Magnetic)	(a)	20	50	75	137				
	(b)	13	45	87	125				
	(c)	13	38	75	150				
	(d)	25	40	87	125				
	(e)	15	55	80	137				
	(f)	13	37	80	125				
Elcometer pull off: (Tinsley pencil)	(a)	13	50	75	125				
	(b)	20	37	62	112				
	(c)	25	43	80	120				
	(d)	20	50	75	120				
	(e)	20	50	70	125				
	(f)	25	45	75	120				
Minitector: (Eddy current)	(a)	20	45	80	150				
	(b)	30	45	70	130				
	(c)	30	40	75	130				
	(d)	25	45	90	120				
	(e)	20	45	70	130				
	(f)	25	40	85	130				
Permascope: (Eddy current)	(a)	20	55	80	140				
	(b)	20	45	87	125				
	(c)	22	45	100	140				
	(d)	15	40	100	125				
	(e)	13	50	100	140				
	(f)	13	40	87	115				

similarly guilty of design faults and if so this would seem to reinforce the view that the paint industry should be more active in advising and educating the architectural profession and designers on the influence of design on practical performance and maintenance.

DR G. de W. ANDERSON (Session Chairman) referred to the automotive field. In his paper, the author had been very kind to the automotive manufacturers and rightly so since they were certainly experts at paint application. Nevertheless, there were still many faults in automotive design, such as inaccessible areas on the inside of car doors, water traps and so forth: in fact, no significant advance had been made in this regard for the last 20 years or so. In addition, vehicle handbooks still gave no positive guidance to the owner in the matter of taking care of paint and bodywork.

MR CLAXTON replied that the question of design was always a thorny problem and this was equally so in the structural steel field, although the professional engineer was probably in a better position to appreciate the faults or shortcomings of a design—even though they still occurred—than the architect, for example, who had to master so many disciplines.

In the automotive field, the continual introduction of new models aggravated the task of minimising corrosion problems at the design stage.

MR Z. KALEWICZ remarked that in order to assemble large parts of constructional steel, it was necessary to obtain a high coefficient of friction. He asked what kinds of paint were used in this country, if any, to solve this problem and whether the author had any experience of zinc ethyl silicate primers.

MR. CLAXTON answered that so far as he was aware zinc ethyl silicate based primers were the only type approved for friction grip priming.

MR K. JULYAN DAY commented that for "faying surfaces (i.e. those connected by high-strength, friction-grip bolts), zinc silicate based coatings were approved treatments. One well-known company, however, had introduced an ethyl zinc silicate which gave results comparable with a coefficient of friction of 0.25, whereas most engineers worked to the BS 3294 recommendation of 0.45, which was easily obtained by most zinc silicates, not only of the ethyl variety.

MR C. E. HOEY said that during his presentation, the author had commented on the inadequacy and impractical nature of many corrosion tests and had shown a slide of boxes enclosed in polythene bags, which he alleged gave after three months results comparable to 10 years' weathering on a bridge. Whilst agreeing that current tests left much to be desired, he wondered how the author could be certain that this test was any different from many other such tests and how did he know that it was equivalent to ten years—presumably this was by evaluating materials of known performance, but he might be evaluating an entirely new material.

The problem was that there were a variety of circumstances (and the same applied to accelerated weathering), and test methods could only approximate them. There would never be a panacea for all situations, and it was up to the technologist to understand the background and to use his judgment to interpret the results of the tests.

MR CLAXTON thanked Mr Hoey for his comments and said he entirely agreed with these. Accelerated tests would always be subject to criticism, although they had to be used.

What was still needed was a set of nationally-accepted performance tests for materials used in the constructional steel industry: the automotive industry had progressed much further in this respect.

With regard to the polythene bag test, experiments were initially carried out with known systems for which there was a long history. Certainly this was the best reasonably accelerated test for multicoat systems which they had found up to the present time.

MR JULYAN DAY commented that in recent tests comparing a number of chlorinated rubber paints, he eschewed accelerated testing, having the time to expose samples on site. Only 12 months was required, however, to sort out those black and middle-chrome yellow paints which did not check or discolour. Out of 14 paint manufacturers, only four supplied panels of both colours which were satisfactory with regard to both gloss and undercoat.

Next month's issue

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

Paints for buildings—the potential and the performance by *P. Whiteley and G. W. Rothwell*

A new versatile lead-free pigment by *S. L. Davidson*

Protection: from hypothesis to principle by *P. J. Gay*

Section Proceedings

South African

Transvaal Branch

High durability colour

A meeting was held at the CIBA-GEIGY Training Centre in Spartan, Johannesburg on 24 July 1975, when Mr C. J. C. Whiston of CIBA-GEIGY Ltd gave a lecture on high durability colour.

The lecturer began with a brief discussion on coating manufacturers' requirements of a pigment for incorporation into a long-life coating.

With a general reminder that pigment behaviour was very dependent upon the resin system and that accelerated weathering could only guide the end user, the results of a project carried out in the Basle Paint Applications Laboratory of CIBA-GEIGY were related.

Seventeen organic and inorganic pigments were tested in eight different coil coating resins at various shade depths for:

- dispersion characteristics
- colour strength
- heat stability
- resistance to industrial atmosphere—Kesternich equipment
- weatherability—4 000 hours Atlas Weather-Ometer WRC 600 Cycle No. 119.

Comments on the slides noted particularly the poorer dispersion of the metal complexes, the high colour strength of the organics, the satisfactory heat stability of all products and the very noticeable differences between the resin systems, particularly with regard to resistance to industrial atmosphere and weatherability.

The weatherability of PVC1 plastisol systems was generally good: thermosetting acrylics gave severe chalking and oil-free polyester showed some chalking. Silicone-modified polyester gave excellent results, organic pigments performing particu-

larly well. With silicone-modified acrylic, chalking was reduced compared with unmodified acrylics.

Results with polyvinylidene fluoride were generally good, inorganic pigments performing well in this system. A modified urethane gave excellent results, organics performing well.

Recommendations made as a result of the investigation could be summarised as follows:

Type of Pigment	Suitability & characteristics
Yellow Ni/Ti complex	Colour strength is weak, tendency to darken in full shade. Satisfactory at 50:50 reduction. Very suitable in combination with organic pigments for lead free matchings
Brown Cr/Fe/Ti complex	Colour strength is weak; good weather resistance including industrial atmosphere
Blue Co/Cr/Al complex	Colour strength is weak, good weather resistance including industrial atmosphere but no advantage over organic blues and greens
Green Co/Ti complex	
Lead based inorganic (scarlets and yellows)	Darken on weathering especially in full shade. The more reduced the less darkening. Poor resistance to industrial atmospheres.
Tetrachloro-iso-indolinone CI Yellow 109	Of use in medium to pale shades.
Tetrachloro-iso-indolinone CI Yellow 110	Excellent pigment—out-performs all other yellow pigments tested.
Flavanthrone Yellow	Only of use below 10:90 colour/titanium dioxide
Azo Condensation Red CI Red 166	Of use in strong shades only—fades 50:50 reduction with titanium dioxide but satisfactory at 80:20 reduction. Combination shades with red iron oxide are an interesting possibility as are combinations with scarlet lead chromes to reduce total lead content.
Thio-indigoid Maroon CI Red 88	This pigment performs well in deep shades above 50:50 colour/titanium

	dioxide—red iron oxide and scarlet chrome combinations offer further scope.
Indanthrone Blue, β-Phthalocyanine Blue & chlorinated phthalocyanine Green	Excellent all-round performance.
Copper-free phthalocyanine Blue	Excellent all-round performance outperforming all pigments under test.

The lecture was spiced with humorous asides and provoked many questions from the floor. A vote of thanks was proposed by Mr R. Millenar and this was carried with acclamation.

P.A.J.G.

West Riding

Aspects of titanium dioxide durability and accelerated weathering techniques

A meeting of the West Riding Section was held on Tuesday 9 September 1975, at the Griffin Hotel, Leeds. Mr G. M. Deighton, of Laporte Industries, presented a paper on the above topic.

Mr Deighton said that his company were carrying out a programme of work designed to improve the degree of correlation between natural and artificial weathering techniques. He discussed the effects which titanium dioxide could have in different types of paint binder and those factors in the design of the pigments (eg surface treatment, type of crystal) leading to these effects.

In the work described, an examination was made on the effect of temperature on the curing of titanium dioxide pigmented paint films in so far as it concerned their durability when subjected to accelerated weathering. This was prompted by the finding that black and white panels in a weatherometer reached different temperatures and this was shown to affect the results of the tests.

Experimental work established that the results were affected by varying the PVC of the paint, as well as by the type of titanium dioxide (surface treated and untreated) used. The main conclusion reached was that at higher PVCs better durability was obtained with a surface treated titanium dioxide at the higher temperatures, whereas at lower PVCs the untreated titanium dioxide gave the better results.

Considering the possibility that the temperature may be affecting the alkyd resin binder used and, therefore, changing the catalytic effect of the pigment a "two layer durability test" was devised. In this case, the exposure panel had a film of paint at its critical PVC covered by a film of unpigmented medium. In these experiments the panels were conditioned at 40°C and 60°C prior to accelerated weathering tests and a range of titanium dioxide pigments were examined. It was found that the temperature during conditioning has a marked effect on the artificial weathering properties. Mr Deighton said that this work was continuing.

A lively and controversial discussion ensued before meeting was brought to a close by a vote of thanks proposed by Mr M. G. Bentley.

R.A.C.

Information Received

Marketing agreement—equipment for spray application

Aeraspray Engineering Co. Ltd, Birmingham, manufacturer of electrostatic and hand-held spray guns for the application of industrial finishes, has concluded an agreement which will result in its equipment being made available throughout Japan and South East Asia.

The agreement has been made with the Matco Manufacturing Co. Ltd of Nagoya, Japan, which will market Aeraspray's range of patented electrostatic powder coating equipment in Japan and South East Asia.

New acrylic plant for BASF

BASF is to erect plant in Ludwigshafen for the production of 90 000 tonnes of acrylic acid per year from propylene. The capital investment costs are estimated at about DM 100 million, including those for the necessary infra-structural measures.

The plant will go on stream in the second half of 1977. At the same time, some of the existing plants will be shut down. The total BASF capacity for acrylic acid will then be 190 000 tonnes per year.

Colour and brightness instrumentation

Evershed Power-Optics Ltd, Chertsey, Surrey, a member of the George Kent Group, has been licensed as sole manufacturer of the range of colour and brightness instrumentation developed by Grafikon (Engineers) Ltd. The first batches of optical colour comparators and electronic colour analysers are already in production, with others to follow shortly.

Evershed Power-Optics will market the

instruments throughout the world to the television and film industries, whilst Grafikon will continue to handle other applications such as those in the paints, dyes, printing and packaging industries.

A new series of publications is being produced by Evershed Power-Optics to cover the existing five Grafikon instruments and other new types under development.

New factory for Winter Osakeyhtiö

Winter Osakeyhtiö, a subsidiary of Oy W. Rosenlew Ab, is to build a new factory at Myllypuro, an industrial district outside Tampere in Finland. The production of both colourants and printing inks will be transferred to the new factory by the end of 1976 after which time only paints will be manu-



Fasson's "FasCal" self-adhesive vinyl and polyester films on this standard 45-gallon steel drum (left) still intact after six winter months' exposure. Twice daily throughout the exposure period, the labels were submerged for eight hours by a tide which runs at up to 3.5 knots and carries a high proportion of disturbed sea-bed silt. Average salinity in the water is 34.5 parts per thousand and the temperature ranged throughout the year from 3 to 20°C. The exposure test site was chosen to offer no protection from wind or sun. A little more than six months' exposure has been withstood by the polythene container (right) put on trial a few weeks before the steel drum and shows the considerable effect of just the tail end of the "fouling" season

factured at the company's present factory in Epilä.

The Myllypuro project will cost approximately 34 million Finn marks (about £4.5 million). The capacity of the new factory is planned to be one million litres of colourants and one million gallons of printing inks per year, and it is proposed that 80 per cent of production will be for export. The year 1974 was the first important year of export for Winter Osakeyhtiö, when the amount exported was five times greater than in 1973.

Unilever expands in Sweden

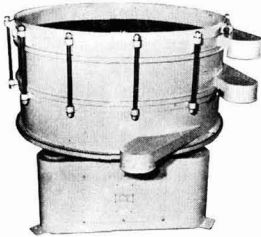
Unilever N.V. has announced that agreement has been reached for the acquisition by a Swedish subsidiary of Unilever of the total issued share capital of Pierre Robert A.B.

Courses

Paint and coatings short courses in USA

The University of Missouri-Rolla is offering several short paint and coatings courses during 1976. The first four will be in January/February and the second four in the autumn. The courses will feature surface preparation, paint application, specifications etc; composition of paints and coatings; paint inspection and quality control; advanced chemical coatings workshop. For further technical information, contact Mr L. P. Larson, Box 3073, Columbus, Ohio 43210, USA.

New products



The new 64-inch diameter separator recently added to the range of Vibrecon vibrating separators manufactured by Gough & Co.

Review

Pigments—Treatise on Coatings

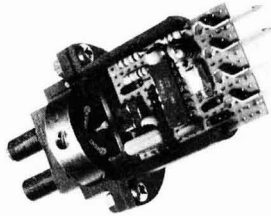
Volume 3 (in two parts).

Part 1 by R. Myers and J. S. Long (Editors).

New York: Marcel Dekker 1975. Pp. xv + 570. Price \$68.00

The editors are well enough known to need little introduction. Perhaps it is sufficient to say that they are a former and the present director of the Paint Research Institute of the USA.

Thirteen authors—all but one American—have contributed the eleven chapters and, arranged alphabetically, these are entitled: Additives, Aluminium pigments, Azo pigments, Calcium carbonate pigments, Carbon black, Chromate pigments, Titanium dioxide pigments, Ultramarine blue.



A cut-out view of the new "Litre meter" flow meter, which can measure flow rates from one drop per 1.5 seconds to 20 litres per minute by counting the revolutions of a minute turbine and sending electronic pulses to a digital or analogue read-out

Improved screen printing oils for indirect printing

The Ceramic Colours Division of Degussa, Frankfurt am Main, has developed screen printing oils for indirect printing, some of whose properties have been considerably improved in comparison with previously-supplied products: the printing and combustion properties of these products have been retained, whilst the compatibility with film solutions has been improved. During tests under operating conditions, only very slight running-off was observed, even with critical colours. The new range consists of four screen-printing oils for the production of glass and enamel transfers, and one screen-printing oil for the production of porcelain and ceramic transfers.

The improved screen-printing oils are already available. Production of the previous types is to be discontinued at the end of 1975.

Bonding agents available on strip steel

Compounding Ingredients Limited, in conjunction with Coated Strip Limited, has produced a variety of thicknesses of steel and aluminium pre-coated with bonding agents and in a condition to be immediately used by the fabricator. The company explains that this is the first time that

bonding agents have been applied by the coil coating technique in the United Kingdom and it should represent a substantial import saving.

Armour Hess agents

Armour Hess Chemicals Ltd has announced changes in its sales arrangements for Denmark and Norway. The company is now represented in Denmark by:

Akzo Chemie Danmark A/S. Hovedgader 26-28, 2970 Hørsholm, Denmark, and in Norway by:

Akzo Chemie Norge A/S. Staaffjaera 9, P.O. Box 132 Kaldbakken, Oslo 6, Norway.

These arrangements are part of the sales reorganisation following acquisition in 1974 of Armour Hess Chemicals by Akzo Chemie BV.

Marine paints

Mr D. M. James, a former Chairman of the Newcastle Section, has kindly sent us a reprint of his contribution on marine paints to the treatise "Surface Coatings" edited by Dr J. S. Long.



A new three-tier model which is being introduced to the range of ball mills produced by the Sharples Engineering Company

There appear to be no indications as to what is intended for Volume 3 Part II, but notable omissions, which might be expected, include: extender pigments, organic pigments (other than azo pigments), and quinacridones.

In the Preface, the editors quite properly mention the book's limitations, directing the reader to Patton's "Pigment Handbook" (see this author's review *JOCCA*, 1974, 57, 120) Presumably their aim is to make the field covered by "Treatise on coatings" comprehensive, but even so it seems difficult to justify this book's appearance at the price. One looks in vain in the subject index for such entries (to be found, for example, in the OCCA Paint Technology Manual Part 6, "Pigments, Dyestuffs & Lakes) as: Anticorrosive, Benzidine Yellow, Covering power, Dispersion, Emulsion, Extenders, Indanthrone Blue, Rutile, Toxicity. The authors on "Lead pigments" and on "Philosophy of colour" give some intriguing historical references that might be difficult to find elsewhere.

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Notes and News

OCCA-28 Exhibition

Alexandra Palace, London. 23-26 March 1976

The continuous dialogue between suppliers and manufacturers in the surface coating industries

The Exhibition, which is known as the international forum for technical display and discussion in the surface coatings industries, is the most important annual event of its kind in the industries and it offers an unparalleled opportunity for a continuous dialogue on technical advances and problems between suppliers and manufacturers in an informal atmosphere.

Many young technologists and scientists who visited the earlier Exhibitions have now risen to high positions within their organisations and the advantage to exhibitors of keeping in constant contact with their counterparts in the manufacturing industries needs hardly to be stressed.

In recent years the Exhibitions have been visited annually by representatives from 50 countries and bringing all these interested parties together at a regular meeting is in itself invaluable when exhibitors consider the cost in time and travel which would be entailed in making personal contact with these visitors each year.

Information in foreign languages

As in previous years, the Association will be circulating information leaflets in six languages, which will contain application forms for those wishing to purchase copies of the *Official Guide* and season admission tickets before the Exhibition.

South African Section

Non-conventional coatings

The South African Section, in collaboration with the Council for Scientific and Industrial Research, announce that their sixth Technical Symposium will be held in Port Elizabeth, South Africa, from 7 to 9 October 1976.

The subject of the Symposium is "Non-conventional coatings", which will cover all aspects of surface coatings technology other than conventional paints. Powder coatings, water-based materials (other than conventional types), non-toxic coatings, cementitious materials, seamless flooring, mastics and sealants may be included. New techniques and developments in surface preparation, application and curing and specialised applications in the auto-

"Official Guide"

This unique publication will contain descriptions of all exhibits and advertising space is available both to exhibitors and those organisations not able to show at the 1976 Exhibition. As in previous years, the *Official Guide* will be published several weeks in advance of the Exhibition so that intending visitors can obtain copies and plan their itineraries.

For the 1975 Exhibition, it was decided that a small charge should be made both for the *Official Guide* and for season admission tickets to the Exhibition. This policy undoubtedly prevented casual visitors who might otherwise be attracted to exhibitions for which no admission charge was made and who gathered quantities of technical literature from the stands. The innovation was welcomed by many exhibitors and in no way acted as a deterrent to visitors to this Exhibition. It is envisaged that a similar charge will be made for the *Official Guide* to OCCA-28.

Each Member of the Association, at home and abroad, will be sent a copy of the "Official Guide" and free season admission ticket.

As for the 1976 Exhibition, copies of the *Official Guide* and season admission tickets will be available several weeks in advance of the Exhibition (*pre-payment only*) from the Association's office and they will

motive, marine and pipe coating industries are suitable subjects.

Authors who wish to present papers are invited to forward a synopsis of approximately 300 words for consideration by the Committee. Such synopses must be received not later than 31 December 1975 and the selected papers will be required by 31 July 1976.

All communications should be addressed to:

The Council for Scientific
and Industrial Research
Symposium Secretariat—S.125
PO Box 395
Pretoria 0001
South Africa.



also be available for purchase at the entrance to the Exhibition Hall.

Full details of advertising in this publication, the basic rates for which are the same as for the *Journal*, can be obtained from the Association's offices.

Alexandra Palace map

Reproductions are available of the two-colour map on page xvii of the area around Alexandra Palace. Members may obtain copies by sending a stamped, self-addressed envelope, marked "Alexandra Palace map" in the top left-hand corner, to the Association's offices.

Technical education stand

In continuance of its interest in the educational field, the Association will once more provide a stand devoted to technical education.

London Section

One-day symposium

The Section will hold a one-day symposium with the Kent sub-section of the Plastics and Rubber Institute at and in conjunction with the Thames Polytechnic, Woolwich, commencing at 9.30 a.m. on Wednesday 19 November 1975. The titles of papers to be presented and the lecturers are given below:

1. "Printing on flexible packaging," by Mr D. A. Fagg of Bowater Flexible Packaging Ltd.
2. "Printing on rigid plastics," by Mr K. Kohlhepp of Hoechst (UK) Ltd.
3. "Vacuum metallising—as a technique," by Mr B. J. Williams of Edwards High Vacuum Ltd.
4. "Decoration of floor coverings," by Mr P. J. Lyon of The Marley Tile Co. Ltd.
5. "Problems in the pigmentation of plastics," by Mr D. M. Varley, of CIBA-Geigy Ltd.
6. "Decoration of plastics with surface coatings," by Dr S. Kut of E. Wood Ltd.

Professional Grade for Ordinary Members

Admissions

At a meeting of the Professional Grade Committee held on 24 September, the following admissions to the Professional Grade were authorised by the Professional Grade Committee:

Fellows

Harold Lomas (*London Section—Ontario Branch*)

Eric Albert André Warner (*Wellington Section*)

Associates

Julian Suriya Surinphong (*General Overseas Section—Thailand*)

David John Murray (*Manchester Section*)

Chettiparambil Achuthankutty Soman (*General Overseas Section—U.S.A.*)

Abdul Monum Khidher (*General Overseas Section—Iraq*)

Transfer from Licentiate to Associate Grade

John Boxall (*Thames Valley Section*)

The innovation of the Professional Grade has proved to be most successful, as evidenced by the impressive list of names which now appears each year in the December issue of the *Journal*.

For the convenience of potential applicants, a chart is reproduced below indicating the different routes to the various Grades.

Full regulations for admission to the optional Professional Grade for Ordinary Members of the Association were last published in the March 1975 issue of the *Journal*. Application forms for admission may be obtained from the Director & Secretary at the Association's offices.

Licentiate ship

It is felt that applicants for admission to the Licentiate grade might wish to have further information on the pattern which it is suggested should be followed for dissertations, the subjects of which have first to be approved by the Professional Grade Committee.

The dissertation should be preceded by a short summary and commence with a brief introduction and some account of the current state of knowledge. Where practicable it should follow the general format of a paper in *JOCCA*.

The dissertation may be a review of a subject, a theoretical treatment, descriptive of practical work or a combination of these. It must indicate that the candidate has a reasonably wide and up-to-date knowledge of his chosen subject and understands the basic scientific principles underlying it, and that he is able to think critically and constructively.

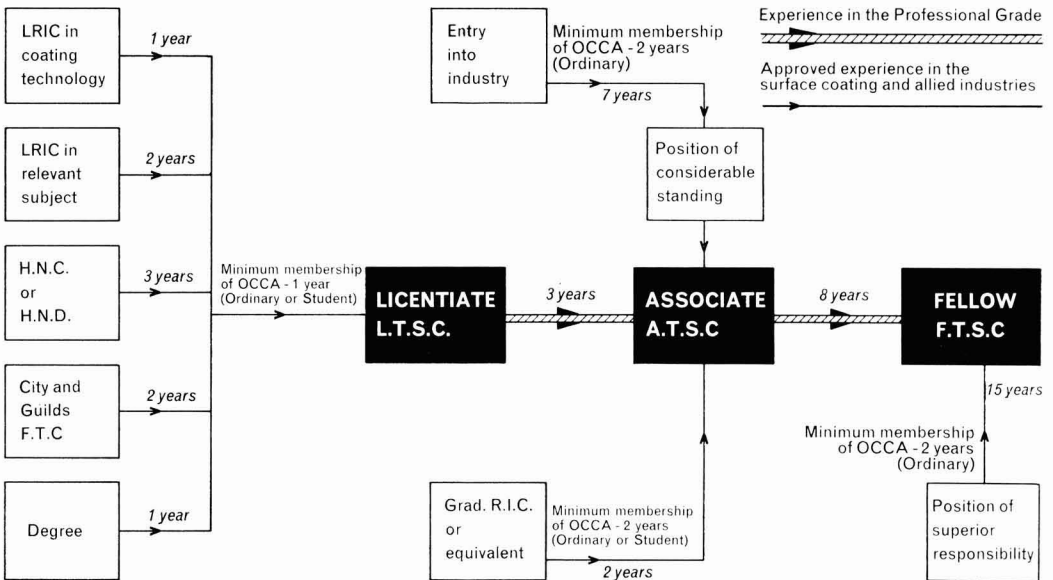
Where practical work is described, some attempts should be made to draw theoretical conclusions or to form some provisional hypothesis, together with an outline of what further work would be required to confirm the views put forward or further to advance the knowledge of the subject.

Where the dissertation is a review or a theoretical treatment, there should be an attempt to contrast and compare any opposing views expressed in earlier works, to examine the views critically, to suggest any compromise interpretation, to account for all the known facts and to outline any further work by which the opposing views could be tested.

Where applicable, references should be given to published work, graphs, diagrams etc. to be appended.

Length: Text should be approximately 5 000 words.

Routes to the Professional Grades



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

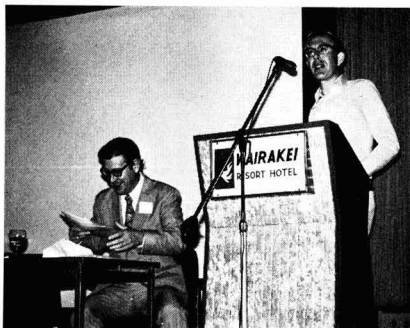
Auckland and Wellington Sections

Wairakei Convention 1975

The 1975 Annual Convention of the New Zealand Sections was held from 1 to 3 August at the Wairakei Hotel on North Island. This was probably the most successful Convention which has been held to date; a total of 210 members and wives attended, and all the papers were of a very high standard.



Mr R. F. Meek (left), Chairman of the Auckland Section, and the Hon. D. MacIntyre, a guest speaker.



Mr G. Dryden (left), another of the guest speakers, with Mr P. F. Sharp, session chairman and Immediate Past-Chairman of the Auckland Section.



Mr F. Wilmshurst (left), a guest speaker, with Mr W. Sell, a member of the Auckland Section Committee.



From left to right: Mr J. F. Beachen, a Vice-President of the Association, and Mr R. F. Meek, Chairman of the Auckland Section, together with Mr O. E. Rutledge. Mr Rutledge holds the Commendation Award certificate, which was authorised by the Council earlier in the year and presented to him at the Convention in recognition of his outstanding work in constant support of the Auckland Section.

News of Members

Dr Marianne L. Ellinger, FRIC, an Ordinary Member attached to the London Section and a Fellow in the Professional Grade, is retiring from her position as Senior Scientist with General and Industrial Paints Ltd (Ault & Wiborg Paints Ltd) which she has held for the last 19 years. It has been announced that Dr Ellinger has been appointed European representative for the Desert Sunshine Exposure Tests Inc of Phoenix, Arizona, the world's largest outdoor weathering facility. She is fully acquainted with the procedures and facilities available.

Mr K. D. C. Bruce, an Ordinary Member attached to the London Section, has joined the Worsdall Chemical Company Limited as sales director and will be responsible not only for sales organisation and outside contacts, but will organise technical service

and generally advise the company on the planning of its products and the use of these materials in printing ink.

Mr Bruce is well known in the ink industry and for many years worked with CIBA-GEIGY specifically on the sale of pigments to the ink industry. Worsdall Chemical Company Limited was founded about four years ago by Mr H. C. Worsdall and is an independent company manufacturing resins for paint and building applications, and also specialising in resins and vehicles for the ink industry.

Mr J. Smethurst, an Ordinary Member attached to the Manchester Section and a Fellow in the Professional Grade, has been appointed a non-executive director of the Silver Paint and Lacquer Company Limited.

Mr Smethurst recently retired after many years as managing director of the pigments

Division of CIBA-GEIGY. Mr L. H. Silver, Immediate Past-President of the Association and chairman of the SPL Group, said in making the announcement that he was delighted to welcome Mr Smethurst to the Board; his experienced knowledge over a wide field could only assist their progressive development. The SPL announcement coincides with the launching of their "Home Charm" range of paints on television, and this campaign will back up what is developing into SPL's most successful year, with sales up some 38 per cent on last year.

Mr M. F. Kooistra, an Ordinary Member attached to the General Overseas Section, has been appointed Manager Advanced Research for Akzo Coatings BV. Mr Kooistra was a former Research Director of Sikkens, Sassenheim, a part of Akzo's Coatings Division.

Register of Members

The following elections to memberships have been approved by Council. The Section to which new members are attached is given in italics.

Ordinary Members

- BECKER, B. KEITH, BSc, 10 Fairholm Place, St. Albert, Alberta, Canada
(London Section—Ontario Branch)
- CHOW, JUSTIN, 1243 Broadview Ave, Apt 304, Toronto, Ontario M4K 2T3.
(London Section—Ontario Branch)
- DO, STEPHEN, Inmont Canada Ltd, 82 Peter Street, Toronto, Ontario M5V 2G6.
(London Section—Ontario Branch)
- JONES, DONALD GEORGE, 191 Dudley Ave, Apt 710, Thornhill, Ontario M3N 2K9.
(London Section—Ontario Branch)
- SCOTT, JOHN L., Box 185, Black Canyon Stage, Phoenix, Arizona 85020.
(General Overseas)

- SEROUSI, RAPHAEL, Tambour Askar Paints Ltd, PO Box 238, Akko, Israel.
(General Overseas)
- TAN, KIM WAH, BSc, 26 Batu Settlement, 4½ Miles, Ipoh Road, Kuala Lumpur, Selangor, Malaysia.
(General Overseas)

Associate Members

- MACDONALD, WILLIAM LEARMOND, 38 Staffs, St. Leonards, East Kilbride, Glasgow.
(Scottish)

Registered Student

- TEOH, YONG SEA, 67 Palewell Park, East Sheen, London SW14 8JJ.
(London)

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication.

November

Monday 3 November

Hull Section: "The factory inspector and industry: partnership is preferable to imposition" by Mr R. V. Souter of HM Factory Inspectorate.

Thursday 6 November

Manchester Section: 50th Anniversary Foundation Dinner, Midland Hotel, Manchester.

Newcastle Section: "Industrial applications of organic titanates" by Dr P. D. Kay, Titanium Intermediates Ltd.

Thames Valley Section: "Treatment and disposal of hazardous industrial wastes" by a speaker from Re-Chem International Ltd.

Tuesday 11 November

Scottish Section—Student Group: "Physical measurements of pigments" by Mr G. Murdoch of CIBA-GEIGY (UK) Ltd.

West Riding Section: "Prospects for surface coating resins in the European market" by Mr C. Martin of Amoco Chemicals Europe.

Thursday 13 November

Manchester Section: Ladies' evening with "Beauty" lecture, at Last Drop, Bolton.

Midlands Section—Trent Valley Branch: Please note that the proposed joint meeting with the Society of Dyers and Colourists has been cancelled.

Wednesday 19 November

London Section: "Decoration of plastics". One-day joint symposium with the Kent Sub-Section of the Plastics and Rubber Institute, to be held at and in association with Thames Polytechnic, Woolwich, commencing at 9.30 a.m.

Thursday 20 November

Scottish Section—Eastern Branch: "Dispersion machinery" by Mr R. Webster of J. C. Forbes Ltd.

Friday 21 November

Bristol Section: "The Health and Safety at Work Act" by Mr J. F. Alcock, HM District Inspector of Factories.

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

Midlands Section: "The outworker" by Mr D. E. Hopper of Ludford Enamelling. *Student lecture.*

Friday 28 November

West Riding Section: Dinner and Dance at the Crown Hotel, Harrogate.*

December

Monday 1 December

Hull Section: "Paint exports" by Mr L. H. Silver, Silver Paint & Lacquer Group, to be held at the George Hotel, Land of Green Ginger, Hull, at 6.30 p.m.

Manchester Section: "The highly flammable liquids regulations" by Mr D. V. Offord, HM Factory Inspectorate, to be held at Woodcourt Hotel, Brooklands Road, Sale, at 6.30 p.m.

Thursday 4 December

Newcastle Section: "High solids, water reducible aminoplast cross-linkers for modern coating systems" by Dr M. Donnez, Monsanto Europe, to be held at the Royal Turks Head Hotel, Newcastle upon Tyne, at 6.30 p.m.

*West Riding Section Dinner and Dance

Tickets for the Dinner and Dance to be held on Friday 28 November may be obtained from Mr Norman Cochrane, 19 Rutland Road, Harrogate, Yorkshire.

Thames Valley Section: "A new approach to large batch milling" by Mr J. Jarvis and Mr R. Ward of Torrance Machinery Ltd, to be held at the Beaconsfield Crest Hotel (White Hart), Aylesbury End, Beaconsfield, Bucks, at 6.30 p.m. for 7.00 p.m.

Friday 5 December

Irish Section: "Car coatings" by Mr A. C. Patrick, Fords of Cork, to be held at the Clarence Hotel, Dublin, at 8.00 p.m.

Tuesday 9 December

Scottish Section—Student Group: "Manufacture of explosives" by lecturer from the Royal Ordnance Factory, Bishopcote, to be held at the CIBA-GEIGY site, Hawkhead Road, Paisley.

West Riding Section: "Aluminium coordination complexes" by Mr J. H. W. Turner, Manchem Ltd, to be held at The Griffin Hotel, Boar Lane, Leeds, commencing at 5.30 p.m.

Thursday 11 December

Scottish Section: "Dispersion and flocculation of titanium dioxide" by Mr J. Rackham and Mr J. G. Balfour, Tioxide International Ltd, to be held at the Beacons Hotel, 7 Park Terrace, Glasgow, at 6.00 p.m.

Thursday 18 December

Scottish Section—Eastern Branch: "Antiquities" by Mr R. Snowdon. *Time and venue to be announced.*

Erratum—OCCA-XXVII Review

We regret that an error has occurred in the Review of the OCCA-XXVII Exhibition, which appeared in the June 1975 issue. On page 230 in the third item in column 2, the maximum speed of Rudolph Meyer's "Tack-O-scope" should read *350 metres per minute*. We apologise for any inconvenience caused.

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We are now developing new resin formulations for spray-applied, water-based paints. We are developing Cardura high solids coatings with good outdoor durability and gloss. And we are developing Epikote powders for automotive primers, drum linings, can coatings and pipe coatings. For more information, please contact your Shell company.*

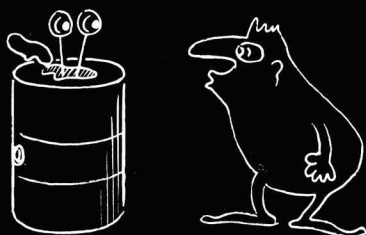


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*In the U.K. this is Shell Chemicals UK Ltd., Villiers House, 41-47 Strand, London WC2N 5LA. Tel: 01-839 9070



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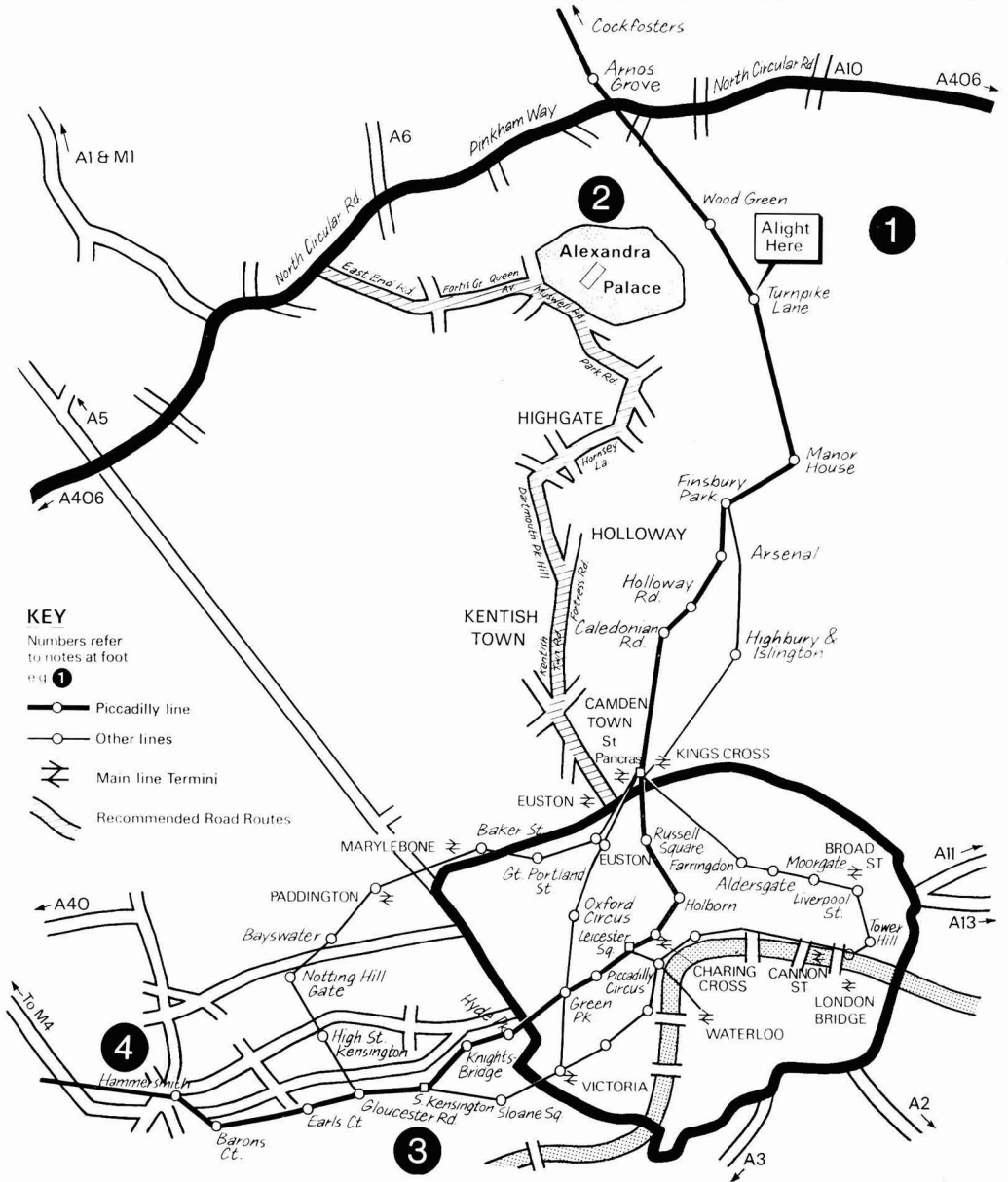
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OCCA-28

For the benefit of intending visitors to the Exhibition, a map is reproduced below of the area around Alexandra Palace showing the mainline stations in central London, the Piccadilly, Circle and Victoria Lines of the underground system and also the road links with the North Circular Road and motorways



1. A free bus shuttle service will operate between Alexandra Palace and Turnpike Lane station on the Piccadilly Line (Underground), which is denoted by the thick coloured line. Destinations of trains may be marked as "Cockfosters" or "Arnos Grove" or "Wood Green".
2. Those travelling by road will find free car parking facilities at Alexandra Palace.
3. Visitors arriving at West London Air Terminal may board the Piccadilly Line trains at Gloucester Road station.
4. At present the Piccadilly Line reaches westward as far as Hatton Cross Station and in 1977 will be extended by the addition of a further station in Heathrow Airport Terminal, so that visitors will then be able to travel direct from the airport terminal to Turnpike Lane station. In the meantime, a bus service operates between the air terminal and Hounslow West station on the Piccadilly Line.
5. The map also shows the position of the main line stations in relation to the Piccadilly Line.

CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of £2.50 per cm. Advertisements for Situations Wanted are charged at 60p per line. A box number is charged at 50p. They should be sent to the Director & Secretary, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF

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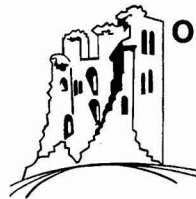
See above for details of rates for Classified Advertisements.



The Oil and Colour Chemists' Association Australia will be organising its first international Paint Convention at Canberra 25-28 September 1977.

The lecture programme, under the heading "Technical & Management Efficiency in the coatings business" will have two concurrent themes—Paint Technology, and Management as it relates to paint manufacture.

The initial circular has been printed and copies are available from N.M. MacLeod, OCCA Australia, Pacific Paint Convention '77, P.O. Box 93 Punchbowl, 2196, Australia.



OCCA CONFERENCE

Scarborough

17-21 JUNE 1975

PRE-PRINTS

Papers given at the Association's Conference 17-21 June under the title "The performance of surface coatings—does the reality match the theory?" are being published with discussions in the *Journal*, and the first appeared in the September issue.

There are, however, a few spare copies of the bound pre-prints available, and these may be purchased at £10.00 per copy (*Prepayment only* to Oil and Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, England).

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Reference : VRT/3/OCCA

- 2 A Paint Technologist aged 25+ with proven experience of **ELECTRODEPOSITION**. Responsibility will cover formulation, customer development formulation, & Q.C. FTC qualification desirable.

Location : Midlands
Salary up to £3,500

Reference : PT/2/OCCA

- 3 A Team Leader for **STRUCTURAL POLYESTERS** — offering wider scope in Laboratory Management. Responsibility will be to the Chief Chemist for R & D, product development with sales and production liaison and some technical service. Age 30-35.

Location : South
Salary £4,000+

Reference : TLSP/5/OCCA

- 4 Two young Paint or Resin Technologists with experience of UV desirably for **METAL COATINGS**. Responsibility in an established team will be to a Senior Development Chemist for product development, advanced customer formulation, product trials and technical liaison with customers.

Location : London
Salary up to £4,000

Reference : PRT/4/OCCA

- 5 Two Technologists aged 20-30 for **AUTOMOTIVE FINISHES**. Responsibility will cover formulation, customer development & customer liaison.

Location : London & North East
Salary up to £3,500

Reference : TAF/7/OCCA

- 6 Two Technical Managers. Aged 30-45. Responsibility is to a Production Manager for materials availability, plant and process development and progressing, with promotion prospects to production management. Qualification HNC+.

Locations : London & North East
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Reference : TM/6/OCCA

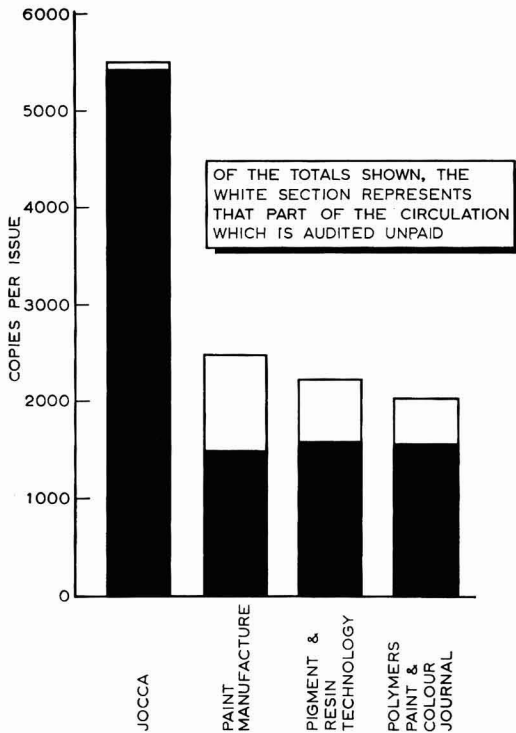
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(Reference Audit Bureau of Circulations Reviews, Jan-Dec 1973)

For full details of advertising in this, and other Association publications, contact C. A. Tayler, Assistant Editor

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Telex: 922670 (OCCA Wembley)

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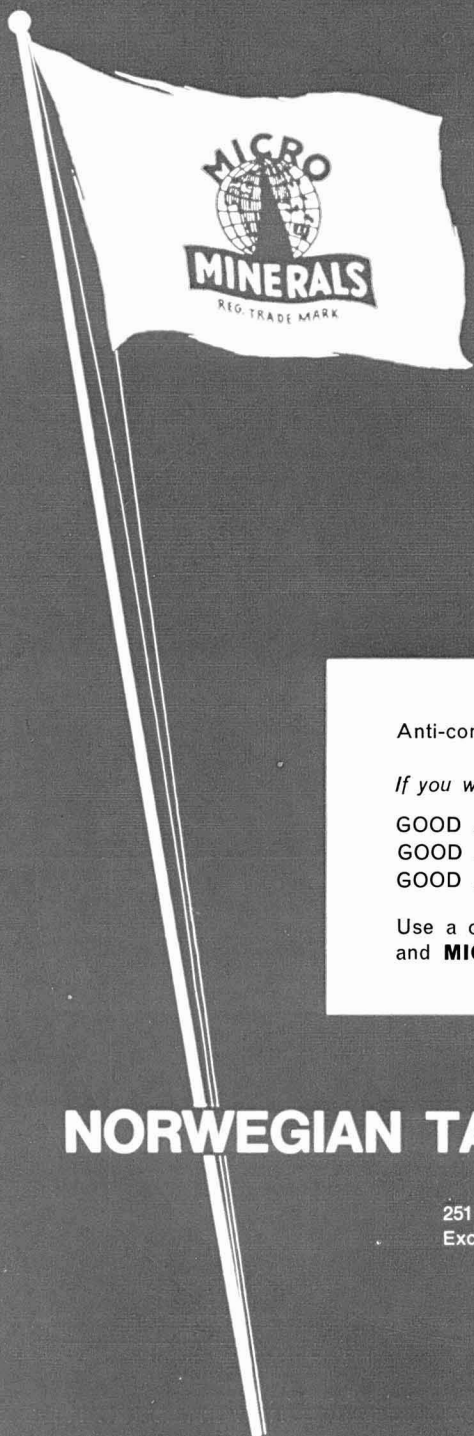
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