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Details on page 270



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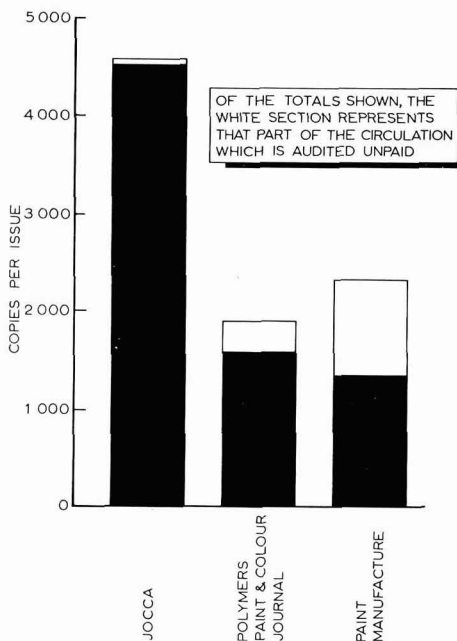
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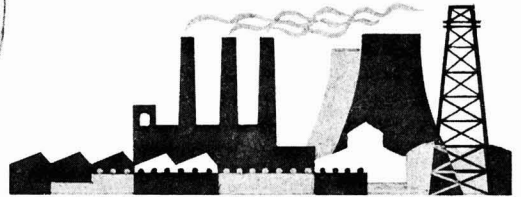
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Vinyl chloride retention in coatings formed from solutions*

By C. M. Hansen

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

Summary

There is no measurable retention of vinyl chloride in coatings formed from solutions. Calculations have shown that this is not anticipated and measurements in practical and exaggerated situa-

tions have demonstrated no measurable ($\ll 1$ ppm) retained vinyl chloride.

Keywords

Types and classes of coatings and allied products

ink
printing ink
foil coating

Raw materials for coatings binders (resins, etc.)

polyvinyl resin

raw materials used in manufacture or synthesis of ingredients for coatings

polyvinyl chloride

Properties, characteristics and conditions primarily associated with:

materials in general

evaporation rate

dried or cured films

solvent retention

La rétention de chlorure de vinyle par revêtements à partir de solutions vinyliques

Résumé

Les revêtements à partir des solutions vinyliques ne retiennent pas de chlorure de vinyle en quantité dosable. Les calculs ont indiqué que ce n'est pas ce que l'on doit s'attendre, mais les

mesures dans la pratique et sous les conditions exagérées ont démontré que la quantité de chlorure de vinyle n'atteint pas à la limite dosable ($\ll 1$ ppm.)

Zurückhaltung von Vinylchlorid in aus Lösungen gebildeten beschichtungen

Zusammenfassung

In aus Lösungen gebildeten Filmen ist keine messbare Zurückhaltung von Vinylchlorid feststellbar. Berechnungen haben gezeigt, dass dies nicht von vornherein anzunehmen ist, und in praktisch

möglichen und übertriebenen Situationen vorgenommene Messungen haben keine messbare Zurückhaltung ($\ll 1$ pro Mio.) von Vinylchlorid gezeigt.

Introduction

Refs. 1-5

Various environmental authorities have focussed their attention on the presence of vinyl chloride monomer (VCM) in food packaging materials. This study was undertaken to explore the amount of retained vinyl chloride which might be anticipated in coatings and inks.

known that the relative evaporation rate³ is a useful practical tool (which correlates with vapour pressure for example) for understanding first stage phenomena. Indeed, extensive studies with a vinyl chloride copolymer (VYHH-Union Carbide) were used to help confirm this fact⁴. The relative evaporation rate compares the rate of evaporation for a given solvent with that of *n*-butyl acetate which has arbitrarily been assigned a value of 100.

Film formation and the evaporation process

Films are formed from polymer solutions by the process of solvent evaporation. This evaporation has been shown to occur in two stages^{1,2}. These are controlled by air surface resistance and internal diffusion resistance, respectively.

The second phase of solvent evaporation occurs over a much longer period of time which is usually called solvent retention. The loss of solvent is controlled by internal diffusion resistance within the film. Transport to the air surface is retarded by polymer molecular segments being required to move to create sufficient space for the solvent molecules to move. Consequently, larger and more bulky molecules move (diffuse) more slowly than smaller or more linear ones and tend to be retained for longer periods of time. Polymer to solvent "bonding" is not the significant retarding effect in this phase as evidenced by an extensive study of this phenomenon which also included numerous data for the

The first stage of the evaporation process is influenced by such factors as solvent vapour pressure, air velocity, and solvent diffusion through a thin laminar boundary layer. It is

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same vinyl chloride copolymer mentioned above⁵. Polymers with lower glass transition temperatures can be expected to retain less solvent (or monomer) because of greater internal mobility. Poly(vinyl chloride) (PVC) is generally plasticised or modified by copolymerisation to allow its use in a solution coating. Such coatings can be expected to retain less solvent or monomer than rigid poly(vinyl chloride), for example.

It might also be noted that the mathematics of diffusion predict a dependence of solvent loss on the square of the film thickness. This means that if a drying film is compared with one of twice its film thickness (at longer times), the thicker film will require four times as long to reach the same level of solvent (or monomer) content as the thinner film. Thus thicker films can inherently be expected to retain more solvent or monomer than thinner films. These relations have also been confirmed experimentally in the experiments mentioned above.

Estimates of vinyl chloride loss during the first phase

Refs. 3, 5-7

The first phase evaporation phenomena are closely related to what in the chemical engineering literature is termed "differential distillation" (distilling solvents in a batch process, for example). The polymer may influence the process to some degree, as will the activity coefficients for the mixtures involved. In a first approximation, however, these will not be considered.

The differential distillation process is described by McCabe and Smith⁶. In the simplest case, mathematical relations are derived for estimating the compositional changes in the liquid film as a function of material evaporated.

The equation concerned is:

$$\left(\frac{N_B}{N_{Bo}}\right) = \left(\frac{N_A}{N_{Ao}}\right)^{\alpha_{BA}} \dots\dots\dots (1)$$

where:

N_B = amount of B(VCM) present at a given stage in the evaporation process

N_{Bo} = amount of B originally present

N_A = amount of A present at a given stage in the evaporation process

N_{Ao} = amount of A originally present

α_{BA} = relative volatility of B to A

The relative volatility can be estimated by a simple ratio of the evaporation rates, but this value is not available for vinyl chloride. In the example below the relative volatility was, therefore, estimated by a ratio of the vapour pressures at room temperature^{3,7}.

$$\alpha_{BA} \approx \left(\frac{P_B}{P_A}\right) \dots\dots\dots (2)$$

Example:

Assuming a typical lacquer formulation having the following composition:

- Vinyl copolymer 25g
- Methyl ethyl ketone 75g
- Vinyl chloride monomer variable

The above mentioned experiments with VYHH have demonstrated that the end of the first phase is associated with a solvent composition of about 0.2g solvent/g VYHH⁵. Thus, the first phase represents a reduction of the volatile content of the lacquer from

3g/g VYHH to 1/15 of this value before entering into the second phase. α_{BA} at 20°C is approximately 2650/71.5 = 37.06 from equation 2.

Substituting these values into equation 1 gives:

$$\frac{N_{VCM}}{N_{VCMo}} = \left(\frac{1}{15}\right)^{37.06} = 2.59 \times 10^{-44}$$

Thus it is clear that theoretically there should be essentially no VCM remaining at the end of the first stage of the evaporation process.

For the sake of including all factors, the data on solvent retention for VYHH cited above indicate that a further reduction of the solvent and/or monomer content present at the start of the diffusion controlled phase will occur to the extent of a factor somewhat greater than two within a reasonable time (hours). Should the temperature be increased above room temperature, the mobility of the polymer chain segments will be increased with an accompanying increase in the diffusion coefficients of the solvent/monomer molecules. A greater reduction in the amount of retained volatile material will result.

Experimental

Refs. 8-11

The analyses for VCM were carried out using a gas chromatograph. For liquid samples with a large VCM content the solvent or lacquer solution was injected directly into the gas chromatograph. When the VCM content was small, the analysis was done by the head space method⁸⁻¹¹. Here the principle is to place the sample in a suitable container, such that a gaseous sample can be removed with a syringe through a membrane without otherwise disturbing the contents. The volatile contents establish an equilibrium in the container and a calibration of the VCM signal by the method of addition allows analysis of the VCM content in the sample itself.

Experimental results—films

A commercially available lacquer with the composition described in the example above was used for these studies. This lacquer was found to have 16ppm VCM based on the nonvolatile portion of the formulation. Films were made in Petri dishes. These were made at an exaggerated film thicknesses of 140 to 180 microns. After 66 hours of drying at room temperature (according to the film thickness squared rule this corresponds to 1.6 minutes for the normal film thickness of 3 microns for this product) no measurable (\ll 1ppm) VCM could be detected in the film.

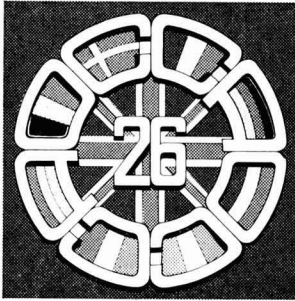
It might also be noted that measurable VCM could not be found in films applied in the manner the product is customarily used *ie* in a film thickness of 3 microns on aluminium foil.

Experimental results—evaporation

Experimental values for α_{BA} were determined by adding 4000ppm VCM to methyl ethyl ketone (MEK) and following the concentration of VCM as a function of the per cent MEK evaporated. Figure 1 shows a gas chromatogram of the VCM/MEK mixture after 4 per cent MEK and 48 per cent VCM are evaporated. Collected results from similar analyses are shown in Figure 2.

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The annual technical exhibition of the Oil and Colour Chemists' Association (known to many simply as “The OCCA”) has become the world's most important event for all those connected with the paint, printing ink, polymer, adhesive colour and allied manufacturing industries. The OCCA exhibition is held every year in London, England. The symbols for the 1974-78 exhibitions were specially designed by Robert Hamblin, Director and Secretary of the Association, to emphasise the very wide coverage which all the Association's activities attract:



The motif for OCCA-26 used the flags of the enlarged EEC converging on the British flag to symbolise the welcome extended to visitors from overseas to the Exhibitions for more than 25 years.



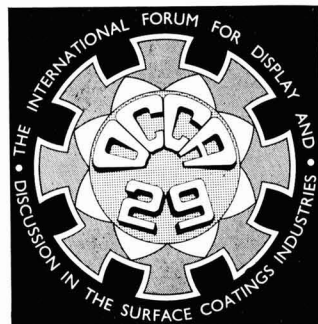
This theme was continued for OCCA-27 by showing the world-wide interest aroused by the Association's annual Exhibitions in London which attract visitors from all parts of the globe.

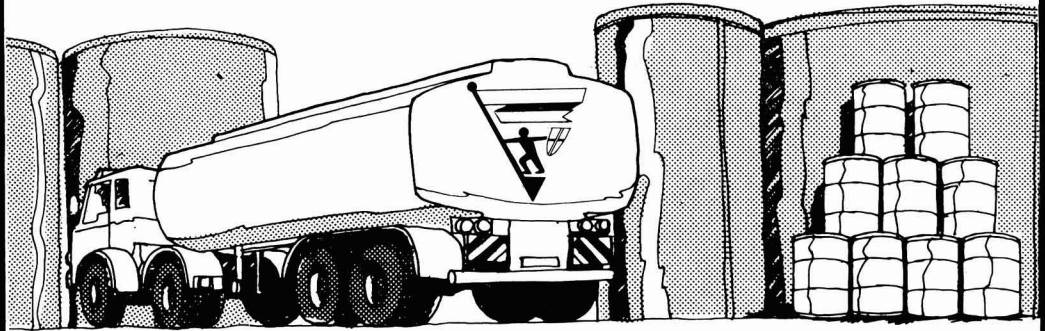


The motif for OCCA-28 emphasised, that the target for 1976 was London where all the Exhibitions have been held, and continued the theme of its international aspect.

letters recall the international aspect of this unique annual focal point for the surface coatings industries, which in 1977 attracted visitors from 250 countries.

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





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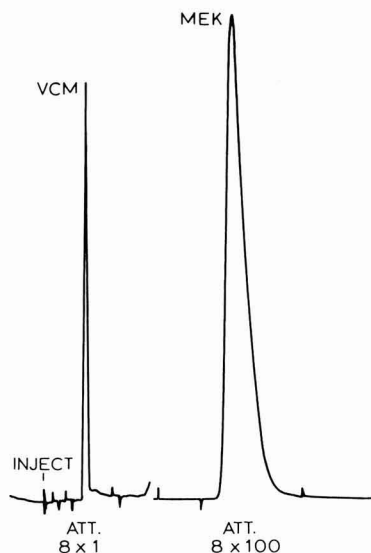


Fig. 1. Gas chromatogram of a 4000ppm solution of VCM in MEK after 4% has evaporated. Calculated VCM content: 2080ppm. Column: 2m, 1/16" id. Porapak Q; Temperature: 170°C; N₂; 30ml/min; Detector: FID; Att: 8×1 and 8×100; Gas chromatograph: Perkin Elmer F 30

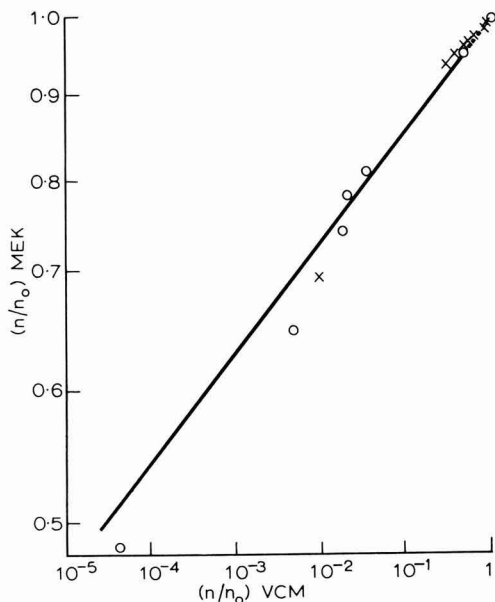


Fig. 2. Evaporation of VCM from MEK, × Initial concentration 4000ppm in MEK, O Initial concentration 25% vinyl resin solids, 75% MEK, 4000ppm VCM (dry resin)

The same evaporation experiment was repeated using the vinyl lacquer formulation described above (25 per cent vinyl polymer). 10 per cent of the MEK in the lacquer was

evaporated and replaced by a solution of about 10 000ppm in MEK. The original VCM concentration was about 4000ppm based on the dry polymer. The experimentally determined concentration of VCM was about 0.2ppm after half of the MEK was evaporated. These results are also included in Figure 2.

Figure 3a shows a gas chromatogram of the head space over a sample of vinyl lacquer after half of the MEK was evaporated. Figure 3b shows a corresponding sample where VCM was added in an amount equal to 1.5ppm based on the dry polymer.

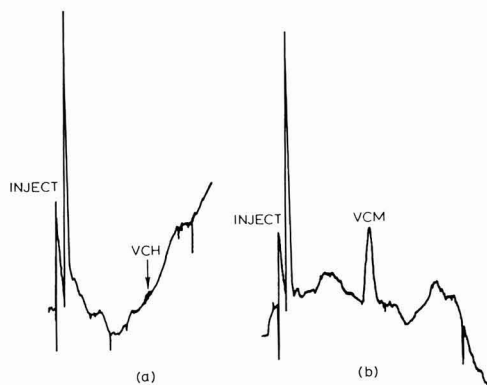


Fig. 3a. Gas chromatogram of the head space over a vinyl lacquer after 50% MEK is evaporated

Fig. 3b. Gas chromatogram of the head space over a vinyl lacquer after 50% of the MEK has evaporated, 1.5ppm VCM added (based on dry solids)

Column: 2m, 1/16" id. Porapak Q, Temperature: 130°C; 10 min prog-20°/min to 200°C; N₂; 30ml/min; Detector: FID; Att: 1×1; Gas chromatograph: Perkin Elmer F 30

Conclusion

As can be seen in Figure 2 there is no significant difference in the evaporation data between the VCM/MEK solution and the VCM/MEK/vinyl polymer solution. In both cases α_{BA} is about 15. Thus it cannot be expected that measurable amounts ($N/N_0 \approx 10^{-11}$) of VCM will be present at the end of the first phase of the evaporation process when the MEK content is reduced to 1/15 of the original amount.

Polymers containing small amounts of VCM are used in coatings applied from solutions. The VCM present in the liquid product will evaporate together with the solvent during the first phase of the film formation process. The dry film will never contain significant amounts of VCM, because the relative volatility will be high regardless of the solvent used. The present results using MEK as solvent justify this conclusion, since MEK is among the most volatile of solvents used and α_{BA} will also be high for any other solvent used.

Acknowledgment

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[Received 25 February 1977]

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Measurement and use of surface tension data in film-forming polymers*

By F. Ewane-Ebele and H. P. Schreiber

Dept. of Chemical Engineering, Ecole Polytechnique, Montreal, Canada

Summary

A thermal gradient bar has been used in the development of a speedy and convenient method for the measurement of critical surface tensions (γ_C) and their temperature dependence for polymer solids. Constant volumes of liquids with known surface tensions (γ_L) are dispensed on to a polymer surface, their contact areas are measured and plotted against γ_L to define the γ_C values. The new method has been shown to produce reliable and reproducible γ_C values for standard polymers, such as polyethylene and polystyrene. In the case of poly(methyl methacrylate) the glass transition temperature was defined by the measurements, and the effect

of specific interactions between polymer and wetting liquid on the glass transition temperature has been demonstrated. Applied to plasticised compounds of a styrene/acrylic copolymer, the γ_C determinations clearly demonstrated the effects of compatibility and incompatibility between polymer and plasticiser. Changes in polymer surface properties due to ageing have been monitored by the present method. The new approach to γ_C measurement promises to be useful for the evaluation of physical interactions among the components of a film-forming system, and for the monitoring of its performance under a wide range of conditions of use.

Keywords

Raw materials for coatings
binders (resins, etc)

polymers

Properties, characteristics and conditions
primarily associated with
materials in general

surface tension
contact angle
wettability
thermal gradient bar

La détermination de la tension superficielle et l'utilisation de ces données dans le domaine des polymères filmogènes

Résumé

Une barre métallique qui incarne des éléments électriques pour assurer un gradient de température a été utilisée dans le développement d'une méthode rapide et convenable pour mesurer, dans le cas des polymères solides, les tensions superficielles critiques (γ_C) et leur dépendance sur la température ambiante. On dégage sur la surface polymère les mêmes volumes des liquides dont les tensions superficielles (γ_L) sont connues, et leurs aires de contact sont déterminées et l'on les fait tracer en rapport à γ_L afin de définir les valeurs γ_C . On a démontré que la nouvelle méthode rend les valeurs γ_C fiables et à la fois reproductibles, dans le cas des polymères usuels, tels que polyéthylène et polystyrène. Dans le cas de polyméthyle méthacrylate, la température de transition à l'état verveux était

définie par les mesures, et également l'influence sur la température de transition à l'état verveux qu'exercent les interactions spécifiques entre le polymère et le liquide mouillant a été démontrée. A l'égard des composés plastifiés à base d'un copolymère styrène/acrylique, les déterminations de γ_C ont démontré clairement les effets de compatibilité et de non compatibilité entre le polymère et le plastifiant. Grâce à la méthode actuelle on a contrôlé les altérations de la surface polymère dues au vieillissement. Cette nouvelle tentative pour la mesure des valeurs γ_C s'annonce utile pour évaluer les interactions physiques parmi les constituants des systèmes filmogènes, et d'ailleurs pour contrôler le comportement de ces systèmes sous une gamme étendue de conditions d'usage.

Messung und Anwendung von Oberflächenspannungswerten in Filmbildenden Polymeren

Zusammenfassung

Eine Wärme-Gradient-Stange wurde bei der Entwicklung einer schnellen und bequemen Methode zur Messung der kritischen Oberflächenspannung (γ_C) und ihrer Temperaturabhängigkeit für Polymerfestkörper benutzt. Konstante Volumina von Flüssigkeiten mit bekannten Oberflächenspannungen werden auf einer Polymeroberfläche verteilt, ihrer Berührungsfächen gemessen und gegen (γ_L) dargestellt, um die γ_C Werte zu definieren. Die neue Methode erwies sich als geeignet zur Erzeugung verlässlicher und reproduzierbarer (γ_C) Werte für Standardpolymere wie Polyäthylen und Polystyrol. Im Falle von Poly-(Methylmethakrylat) wurde die Glasübergangstemperatur durch die Messungen definiert, ausserdem wurde die Wirkung der spezifischen Reaktionen zwi-

schen Polymer und Netzmittelflüssigkeit auf die Glasübergangstemperatur aufgezeigt. Die γ_C Bestimmung, angewandt auf weichgemachte Verbindungen eines Styriols Akrylat-Kopolymer, erwies deutlich die Auswirkungen von Verträglich- und Unverträglichkeit zwischen Polymer und Weichmacher. Veränderungen in den Eigenschaften der polymeroberflächen zufolge Alterung wurden mit Hilfe der beschriebenen Methode überwacht. Die neuartige Verwendung der γ_C Messung verspricht für die Beurteilung physikalischer Reaktionen zwischen den Komponenten eines filmbildenden Systems und für die Überwachung seines Verhaltens unter zahlreichen Anwendungsmöglichkeiten nützlich zu sein.

Introduction

Refs. 1-9

This paper is concerned with the measurement and use of critical surface tensions, γ_C , and their temperature dependence for film-forming polymers. The methods used were developed for convenience and for routine use in practical cases, rather than for the highest accuracy. The motivation for this work lies in part in the pressures arising from the consumer- and environment-oriented society. These create a challenge to

many fields of science and technology, and not least to the area of protective coatings. The need to provide high performance at economically permissible costs is taken as a matter of course. Serious new complications in the formulation and use of coatings arise as a result of legislative rules concerning the emission of volatiles, the generation of odour etc. The steadily increasing costs of raw materials also must be included in this short list of challenges to the coatings technologist.

In response to these challenges a widely used approach is

*The lecture given to the London Section on 16 November 1976 at the Sheraton Heathrow Hotel was based on the work described in this paper.

to develop new film-formers, to modify formulations, and generally to apply the concepts of synthetic organic chemistry and polymer science. Invaluable though these approaches are, they do not by themselves guarantee that optimum performance will be realised from any given composition. To do so also requires an understanding, and hence an adequate control, of complex physico-chemical forces which exist in a film-forming system. The thermodynamics of interaction involving the components are among the principal of these forces and may well be critical for the determination of performance effects, such as adhesion, gloss, flow, durability, etc. A fuller understanding of the physico-chemical phenomena occurring in the formation and use of coatings, therefore, ranks as a priority objective in meeting future challenges. The present paper contributes to that goal.

It is not novel, of course, to note the need for useful measurements of component interactions in coating systems. Coatings being traditionally solvent-borne, the relevance of solution thermodynamics, and particularly its extension to polymer solutes, has long been recognised. A particularly well-known tool of the coatings technologist is the solubility parameter. Derived from the theory of regular solutions¹, it was quickly developed into a guide for solvency and co-solvency in solute-solvent mixtures^{2,3,4}. In practice, matching up solubility parameters produces good results (compatibilities) when the components are non-polar and when interactions arise mainly from van der Waals forces. Difficulties arise, however, when polar forces are involved in the interaction balance; furthermore, as the solubility parameter is fundamentally related to an energy of vapourisation¹⁻⁴ (a quantity which is experimentally inaccessible for most film-forming polymers), in practice one must resort to calculations⁵ and interpolations⁶, and these involve serious assumptions. The situation has given rise to a profuse literature, and this has been well reviewed recently by Barton⁷. Numerous modifications of the basic solubility parameter concept have been introduced to cope with these problems and there is little doubt that practical use of the solubility parameter is here to stay. Equally, however, it is difficult to imagine that the parameter is the universal and optimum guide for the coatings technologist.

A particular problem of concern in the performance of coatings, and one which is not well handled by the solubility parameter approach, is the time-dependence of polymer properties. That is to say, the physical properties of polymer solids and solutions are not necessarily uniquely defined by composition and by the independent variables of the system. Instead, they may vary with time, as thermodynamic or morphological steady-states are attained. Thus, Rudin and co-workers have reported changes in properties of dilute polymer solutions⁸ as the solutes slowly aggregate, driven by thermodynamic forces. Work in the authors' laboratories has shown⁹ that adhesion properties at solid polymer-polymer interfaces are strongly dependent on the thermal history to which the interface is subjected; time and temperature-dependent crystallographic effects being a controlling factor in the adhesion characteristics. Protective coatings, in practice, are expected to perform well for long periods of time; they may be subjected to extreme variations in temperature, composition of the surrounding environment, etc. Variables are, therefore, in force which may compromise the validity of compatibility evaluations made under fixed conditions, for example when applying the solubility parameter concepts. Clearly, to optimise the properties of coatings for the range of conditions to which they will be subjected, it would be useful to define experimental measurements of component interactions, still based upon thermodynamic principles, but suitable for repetition as the product

ages or as it is subjected to varying environmental constraints. For these reasons the use of the critical surface tension and its temperature dependence is proposed as one route to the desired goal, and a simple empirical and convenient method of measuring the desired quantities is described in this paper.

Polymer surface tension and its temperature dependence

Refs. 10-19

The imbalance of forces existing at any interface separating solids, liquids or vapour gives rise to a surface free energy or surface tension, the magnitude of which is a characteristic of the materials in question. In terms of measurable quantities, the surface free energies may be obtained from the contact angle, θ , of a liquid in equilibrium with its vapour, and in contact with the solid. The required relationship is given to a reasonable approximation by Young's equation:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \dots \dots \dots (1)$$

where γ is the surface tension and the subscripts *S*, *L*, and *V* refer to solid, liquid and vapour.

Although the surface free energy of a polymeric solid, such as that of a coating, would provide an excellent "fingerprint" of the material, this quantity is nearly impossible to evaluate absolutely. Analogous with the problems encountered with the solubility parameter, here the effects of molecular weight distribution, different tacticities of polymer chains, etc. combine with more general problems of surface roughness, contact angle hysteresis, etc. to complicate the determination. Excellent reviews are available for fuller treatments of this complex subject^{10,11}.

An experimentally attractive solution to the problem is provided by the work of Zisman and co-workers¹². Here the contact angle is measured for a series of liquids with known γ_{LV} on a polymer surface. In many cases a straight line relationship is observed when $\cos \theta$ is plotted against γ_{LV} and this allows the definition of a limiting or "critical" surface tension, γ_C , as given by the expression:

$$\cos \theta = 1 + K(\gamma_C - \gamma_{LV}) \dots \dots \dots (2)$$

where *K* is the limiting slope of the linear relationship. It is noted that the critical surface tension of the solid, γ_C , is not equivalent to the solid's surface free energy. Nevertheless, it is a very convenient way of classifying the surfaces of polymeric solids, and it has been determined extensively for polymers ranging from the fluorocarbons¹³ to the high-energy extension of polymers such as polyamide-epichlorohydrin resins¹⁴. Its use as a characterisation parameter for complex organic coatings is indicated.

The temperature dependence of γ_C appears to be a related variable of real value to the characterisation of polymer surface properties. There is no universally accepted theory to account for the behaviour of $d\gamma_C/dT$, but considerable empirical success has been reported in linking this differential of γ_C with corresponding changes in the free volume of the polymer. Of the pertinent accounts of the close relationship between these variables, those by Roe^{15,16} and Patterson and co-workers^{17,18} are particularly to be noted. Specifically, Roe has suggested a relationship between γ_C and the parachor, *P*, of a polymer segment:

$$\gamma = \left[\frac{P \cdot \rho}{M} \right]^4 \dots \dots \dots (3)$$

where ρ is the density and M the molecular weight of the segment. Clearly, it would be expected that the temperature dependence of surface tension would be very slight and monotonous as long as no phase transitions or abrupt compatibility shifts take place in the temperature range investigated. Thus, $d\gamma/dT$ should prove to be a sensitive measure of precisely those events which could seriously alter the performance of a surface coating. An extensive review of the temperature variation of γ_C and of contact angle measurements, which is pertinent to this work, has been given by Neumann¹⁹. The remainder of this paper is concerned with experimental evaluations of γ_C and $d\gamma_C/dT$ in film-formers.

Experimental

Ref. 19-21

The intention of the authors was to provide for rapid measurement of both γ_C and $d\gamma_C/dT$, preferably in one operation. The conventional determination of contact angles seemed ill-suited to this purpose; Neumann's approach¹⁹ whilst ingenious and accurate, appears to be beyond the reach of many industrial laboratories. The simpler approach, documented below, was therefore followed.

Apparatus

The device used to determine the desired quantities is a thermal-gradient-bar (tgb). The tool is well known and used in the protective coatings field, and has been previously described in the literature^{20,21}. In this version, shown in Fig. 1, and produced in the McMasterville laboratories of Canadian Industries Ltd., a 40.6 cm x 7.6 cm x 2.8 cm aluminium bar is mounted in a hard asbestos base. The bar is centered on ball-bearings and recessed so as to allow a glass sheet to cover the unit. At one end of the bar, an aperture is drilled into the asbestos block to accept a standard cartridge heater (300W used in the work being described), whilst at the other end provision is made for the circulation of coolant (for example, tap water maintained at constant pressure head). A thermistor temperature controller was used with the heater to offset line voltage fluctuations and maintain a linear, constant temperature gradient along the apparatus. A variable resistor controlled the heat input. Absolute temperature readings are provided by seven thermocouples, placed in contact with the metal bar at regular intervals.

with the aluminium bar. Circular magnets located at 2.5 cm intervals along the long edges of the bar promote close metal-to-metal contact. To achieve thermal equilibrium more rapidly a light layer of non-melting (silicone) grease is applied to the back of the test panels. Placing the metal panel on the tgb produces a thermal disturbance of about 3°C, which is corrected in about 5 min. Figure 2 shows typical linear temperature distributions for the tgb in operation. Curves (i) and (iii) differ in the resistor setting used (115V for i; 80V for iii), whilst the shallow gradient of curve (ii) was produced by replacing (as coolant) tap water with water heated and regulated at 40°C. In operation, the temperatures at each measuring station remained within 1°C for periods in excess of 5 hours. The apparatus can also be used for isothermal operation by balancing the heat flux at either end of the metal bar. Reliable isothermal operation has been demonstrated up to about 50°C.

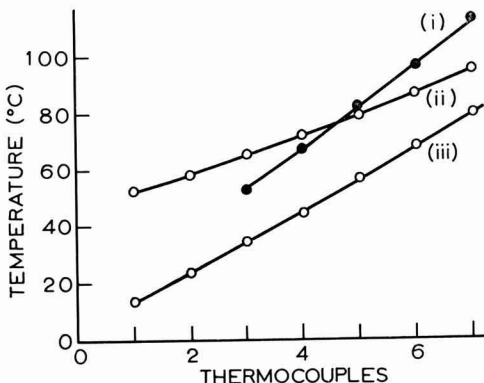


Fig. 2. Typical linear thermal gradients at steady-state operation. Curves i) ii) and iii) correspond to different heat flux conditions. See text for detail

Procedure

Ref. 12

For the determination of surface tension parameters, a desired temperature gradient was first established on the tgb. Polymer coatings were then prepared on metal (Bonderite) panels, these were set on the bar and the assembly was brought to a thermal steady-state (about 10 min). Liquids of known γ_{LV} were then dispensed on to the polymer surface from 50 μ l (Hamilton) microsyringes. Generally, a series of four or five test liquids was employed and a vertical array of droplets was placed in a constant temperature band ($\pm 1^\circ$ C) on the surface. Typically 4-6 such groups of drops were distributed over the length of the specimen, to define the temperature effects at intervals of about 10°C. The experimental arrangement is illustrated in Fig. 3. Here

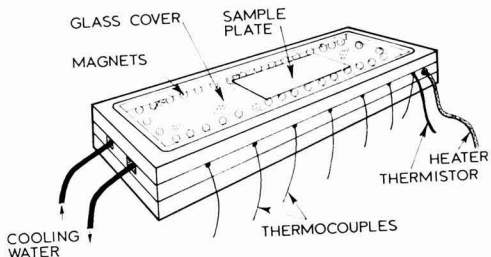


Fig. 1. Diagram of thermal gradient bar, showing heat flux and detection installations

In use, standard metal panels, 5.7 cm x 17.1 cm or 5.7 cm x 34.3 cm bearing the surface coating are placed in contact

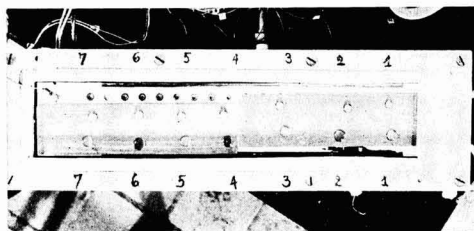


Fig. 3. Illustration of arrangement for γ_C and $d\gamma_C/dT$ measurement. Liquids placed in isothermal bands

two panels are placed end-to-end and, for simplicity, only a pair of liquids is used to trace the temperature dependence of surface properties.

As soon as the droplets have been placed on the polymer surface, the tgb is covered with its glass sheet and a temperature steady-state is re-established (2–3 min.). The area of the deposited droplets is then measured either directly or, as in this case, by photographing the assembly. This provides a permanent record of the situation. If several liquids are to be used simultaneously, care should be taken to use relatively non-volatile materials, so as to avoid complications arising from evaporation losses or vapour-phase interactions. On the other hand, the area of droplets can be recorded as a function of time so as to:

ensure that a steady-state value of the contact area has been established

trace variations in contact areas due to solid-liquid interactions

follow time—and temperature—dependent variations in polymer surface properties.

The droplet area, A , can be measured accurately from photographs, with a planimeter. Since the volume of droplets dispensed is always constant, the area is directly proportional to the contact angle. A minimum contact area will be read when the contact angle is 90° , that is, when the liquid is non-wetting and the droplet will be hemispherical with a circular contact of radius r_o . Maximum contact area will correspond to a contact angle $\theta = 0^\circ$ and a contact circle with radius r_m . The relationship between the limiting radii of the contact circle is of the form

$$r_m = r_o (1 + k \cos \theta) \dots \dots \dots (4)$$

but the value of k is not necessarily unity. Analogous to the procedure used in Zismann's approach to γ_C measurement¹², an estimate of γ_C is possible by plotting the measured droplet area against γ_L , and extrapolating the rectilinear band to an area value corresponding to $A_{lim} = \pi r_m^2$. In practice, however, we have found it preferable to calibrate the apparatus with polymer solids of known γ_C and establish A_{lim} empirically. This avoids the need to define r_m experimentally, since to do so would require coping with problems of surface non-uniformity, an occasional absence of clear boundaries at liquid/solid interfaces for strongly wetting liquids, etc.

Apparatus calibration

Ref. 22

Branched polyethylene (PE) and polystyrene (PS) were the low surface energy polymers selected for calibration purposes. Both of these materials have been used frequently in γ_C studies and accurate values of the parameter have been reported²². The low-density PE used here was manufactured by Canadian Industries Ltd, had a reference density of $0.9188 \text{ gm cm}^{-3}$, and a melt flow index of 2.0. The PS sample had a molecular weight of 8.6×10^4 as reported by the manufacturer, Dow Chemical Co.

Films were prepared for γ_C evaluation by both the new tgb method and by the standard contact angle approach. Test specimens were compression molded against Bonderite, using a PTFE (Teflon) sheet as the upper, non-adhering molding surface. Contact angle data at 25°C were measured

with the Imass Contact Angle Analyzer, using the following wetting liquids:

Contact fluids	γ_L (dyne. cm^{-1}) at 25°C
1-2 propane diol	34.1
Nitrobenzene	41.5
Ethylene glycol	47.7
Glycerol	63.4
Water	72.8
*Chlorobenzene	33.2
*Toluene	28.2
*Butyl benzyl phthalate	40.4

The liquids marked with asterisks were not used in the calibration sequence itself, but were involved in subsequent experimental runs, hence their inclusion here. All fluids were reagent grade and were used as supplied by manufacturers.

The same polymer-liquid pairs used for contact angle work were also involved in tgb experiments carried out isothermally at 25°C . Literature values of γ_C and those obtained from the present contact angle measurements are compared below:

	γ_C (dyne. cm^{-1}) at 25°C for:	
	PE	PS
Literature ²²	29—31	30—36
This work	30.7	34.5

This data can be accepted as typical for the polymers in question, and these values were therefore used to define the required A_{lim} , as shown in Fig. 4. This shows the contact area vs γ relationship for PE [curve (a)] and PS [curve (b)] as given by the tgb and defines $A_{lim} = 1.71 \pm 0.01 \text{ cm}^2$. The stated A_{lim} value was used throughout this work to obtain the desired γ_C information at all temperatures. The procedure is based on the assumption $d\gamma_C/dT$ and the droplet area changes due to the thermal expansion of the test liquids are compensating effects, at least in terms of the accuracy of present measurements. For non-interacting solid-liquid pairs, this assumption appears to be very reasonable.

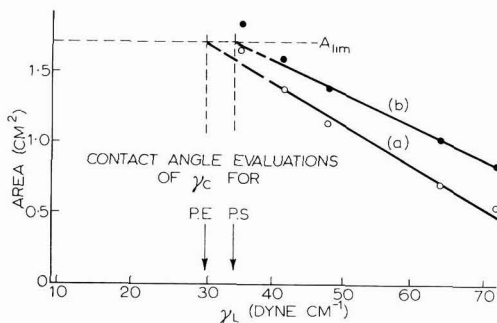


Fig. 4. Contact areas vs γ_C for calibration liquids on standard polyethylene (a) and polystyrene (b) substrates. Horizontal broken line defines A_{lim}

Materials for exploratory work

In the exploratory section of this work, two film-formers were employed. One was polymethyl methacrylate (PMMA)

homopolymer, with a viscosity-average molecular weight $M_v \approx 4.2 \times 10^4$. The second was a styrene, methyl methacrylate, methacrylic acid (S/MMA/MAA) copolymer with the overall mole-composition ratio 80/15/5. Both polymers were produced by Paint Research Laboratories, Canadian Industries Ltd. In a number of cases butyl benzyl phthalate (BBP) and glycerol dibenzoate (GDB) were used as external plasticisers for the copolymer. In these cases the plasticisers were added by mixing the polymer powder with the liquids in a Brabender Plasticorder at 60°C.

Results and discussion

Some characteristics of PMMA

Refs. 15-17, 19, 23, 24

The γ_C at 25°C for the present PMMA sample was determined from isothermal tgb experiments using non-swelling fluids taken from those listed above. The plot of droplet area vs γ_L is shown in Fig. 5. It defines γ_C at the intersection of the linear portion of the relationship and the A_{lim} line, and assigns to the polymer a $\gamma_C = 38.1$ dyne cm^{-1} . This is in good agreement with the range of γ_C values reported for PMMA²³, and further confirms the validity of the tgb method as a route to critical surface tension data.

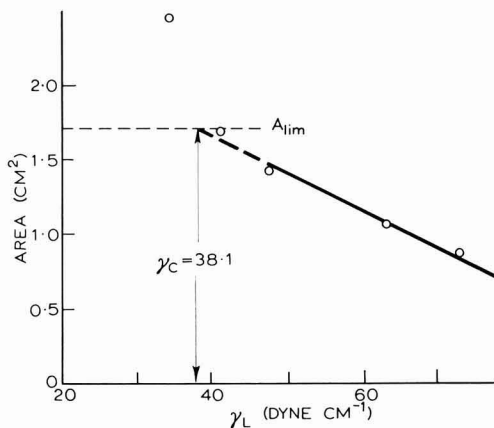


Fig. 5. Droplet area vs γ_C for PMMA at 25°C

The same polymer was next used in evaluations of γ_C in the temperature range $25 < T < 110^\circ\text{C}$. Figure 6 presents two sets of information relating to this part of the study. In addition to the actual γ_C vs T representation, two sets of droplet area vs T data are given in Fig. 6, one curve relating to glycerol as the wetting liquid, the other to toluene. The temperature variation of γ_C follows the expectations of theory^{15,16,17,19} and is consistent with other experimental observations of the temperature dependence of γ_C for polymers¹⁹. A shallow, linear relationship is defined in Fig. 6. This, however, also displays a temperature range in which distinct non-linearity occurs. Extending the high-temperature portion of the linear relationship as indicated in Fig. 6, defines the limit of the higher-temperature-range linearity at $97 (\pm 2)^\circ\text{C}$. This is associated with the glass transition temperature of the polymer, T_g and it is suggested that this principal transition in the polymer occurs over a temperature range of about 12–15°C, that is the extent of non-linearity in the data of Fig. 6.

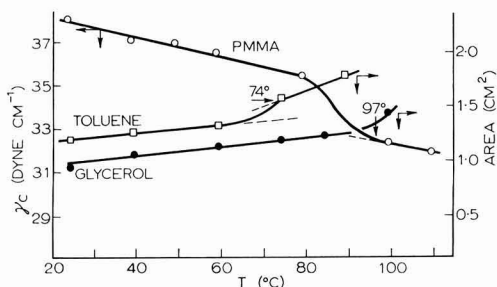


Fig. 6. The temperature dependence of γ_C for PMMA; contact area vs T showing sensitivity to specific interaction between solid and toluene

The T_g value of about 97°C is again defined in the droplet area vs T curve for glycerol. Glycerol can be taken as a non-swelling (non-interacting) liquid for PMMA, and thus it is assumed that at each temperature a steady-state value of the droplet area has been recorded. Clearly, the response of the polymer to thermal effects at T_g is reflected in a decrease of surface tension and hence in a marked deviation from linearity in droplet area. A very different situation is portrayed by the toluene data. Toluene is a known solvent for PMMA at temperatures greater²⁴ than about 10°C , hence the interaction between the film and the contact liquid may be expected to affect the results of tgb experiments. Indeed, it is noted that at each temperature on the range studied, the contact area of toluene is significantly greater than that of glycerol. In addition, the deviation from linearity in the area vs T plot now occurs some 25° below the apparent T_g . Evidently, the solvent action at the liquid-solid interface has produced a quasi-plasticisation resulting in a significant decrease in the local transition temperature.

The data in Figure 6 illustrate the usefulness of the present experimental method as a means of detecting polymer transition temperatures. More importantly perhaps, the method is seen as a means of specifying the existence of strong interactions between substrate and wetting fluid, and that over a significant temperature range. An important note of caution is also associated with these data, since for any polymer-liquid pair there can be no *a priori* guarantee that steady-state, or "true" values of the contact area are being recorded. Such parameters as T_g read from the data, must therefore also be viewed with caution. The demonstration of the dependence of this parameter on polymer-liquid interactions, and the implied usefulness of the present measurements as a guide to the performance of coatings in selected use environments (liquid or vapour), should, however, more than offset this difficulty.

Surface characteristics of copolymer

Refs. 6, 7, 13, 23

The critical surface tension of the S/MMA/MAA copolymer was first defined at the reference temperature of 25°C by isothermal tgb experiments in which 1–2 propane diol, nitrobenzene, ethylene glycol and glycerol were the contact fluids. A value of $\gamma_C = 34.0$ dyne cm^{-1} was obtained. This is within experimental error of the PS value and suggests that internal plasticisation effects due to the minor constituents lead to (surface) relaxation which offsets the inherently higher γ_C values of acrylic polymers^{13,23}. The temperature variation of γ_C , determined in the range 25 – 90°C through use of the same wetting liquids, is shown in Fig. 7. The

relationship is not linear but instead shows slight downward curvature which becomes more accentuated at temperatures above about 70°C. Assuming the test liquids to be non-solvents (there was no evident swelling of the copolymer by any of the four liquids used), no major phase transitions appear to occur in this material within a temperature interval roughly consistent with use conditions. The reasons for curvature in the relationship of Fig. 7 cannot, however, at this stage, be discussed in greater detail.

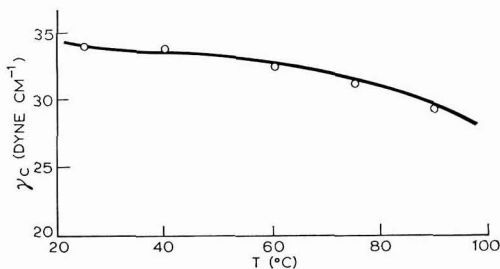


Fig. 7. Temperature dependence of γ_C for S/MMA/MAA copolymer; as determined by tgb method

The copolymer was next used in a series of plasticised versions, with BBP and GDB as candidate plasticisers. The purpose of this exercise was to indicate the sensitivity of the γ_C measurement to plasticisation effects, and to the effectiveness of two distinct plasticising liquids. In this report only data at 25°C are considered; these pertain to the polymer containing up to 25 per cent (by volume) of each plasticiser. A more detailed account of the surface tension vs plasticisation sequence will be presented elsewhere. The pertinent results are listed in Table 1.

Table 1

Critical surface tensions (25°C) for variously plasticised copolymer compounds

Polymer	Composition (%)		γ_C (dyne. cm ⁻¹)
	BBP	GDB	
100	0	0	34.0
95	5	0	29.5
95	0	5	35.8
85	15	0	30.2
85	0	15	37.3
75	25	0	31.5
75	0	25	40.7
0	100	0	40.4
0	0	100	41.5

It is to be noted that the pure plasticisers have similar γ_L values so that interfacial tensions at polymer/liquid contacts should be roughly equivalent for these materials. Similarly, simple solubility-parameter (δ) calculations would not lead one to expect major differences in plasticisation effectiveness, since BBP and GDB have parameter values⁷ in the range 10–12 (cal. cm⁻³)^{1/2}. Differences would, of course, be expected in the associative force contributions to δ in these liquids, the glycerol derivative being more strongly hydrogen bonding and more strongly subject to polar force interactions. The results in Table 1, however, show a radical difference between the behaviour characteristics of the two plasticisers. Moreover, these differences in behaviour are strongly evident even at five per cent liquid content. The addition of BBP results in an initial slight drop in γ_C ; syste-

matic but minor increases in γ_C occur as the volume of BBP rises to 15 and 25 per cent. The data may be viewed as reflecting an initial relaxation of surface tension due to the solvating effect of BBP. Thereafter γ_C increases (presumably) toward the corresponding value for the pure liquid. Thus, the γ_C /composition variation appears to be that of a compatible system which has surface tension properties distinct from either of the constituent materials.

In contrast, the γ_C data for polymer/GDB mixtures show a rapid rise toward the value for pure plasticiser, falling roughly within experimental error of that datum at 25 per cent GDB content. The conclusion to be drawn from the result is that at the temperature of measurement (25°C) the wetting liquids probing the energetics of the polymer substrate are predominantly in contact with the GDB component. Exudation of the plasticiser to the surface of the polymer is a suggested occurrence. The implication, therefore, is that GDB is not a suitable plasticiser for the present polymer, being incompatible with it at volumes as low as five per cent.

Finally, the results of an experimental sequence designed to test the usefulness of the present approach to surface property determination for the detection of ageing effects in polymer films are reported. Tgb experiments were, therefore, performed on samples of PMMA, S/MMA/MAA and on the copolymer containing 15 per cent BBP, which had been aged up to 72 hr. on the gradient bar. The temperature range covered in this series by the tgb was 25°–70°C, but γ_C evaluations were made only at isothermal stations of 25°, 40° and 60°C. The data are given in Table 2. In all cases γ_C values refer to the same temperature used for ageing the specimens.

Table 2

Time dependence of γ_C in coating compositions at various temperatures

γ_C (dyne. cm⁻¹) following ageing at:

	25°C	40°C	60°C
PMMA			
t = 0	38.1	37.0	36.7
t = 1 hr	38.0	37.4	37.0
t = 5 hr	38.2	36.9	37.3
t = 24hr	38.4	37.5	37.1
t = 72hr	38.0	37.6	37.7
S-MMA-MAA			
t = 0	34.0	33.1	32.6
t = 1 hr	33.7	33.3	33.1
t = 5 hr	34.4	33.7	33.9
t = 24hr	34.3	35.1	35.2
t = 72hr	33.9	35.8	36.7
Copolymer + 15%BBP			
t = 0	30.1	29.5	29.0
t = 1 hr	29.9	29.8	28.1
t = 5 hr	30.4	29.1	28.7
t = 24hr	30.4	29.6	28.4
t = 72hr	30.8	30.0	29.3

PMMA: The homopolymer appears unaffected by lengthy exposure to elevated temperatures, although a very slight increase in γ_C appears to be noted at 60°C. The shift is sufficiently systematic to suggest incipient instability of the polymer at this temperature. Oxidative changes may be suggested, though in the absence of quantitative analytical data, this remains a speculation. At any rate, the experiment does warn of potential changes in film properties resulting from prolonged residence at temperatures at or above 60°C.

S/MMA/MAA: The results here are more complex and consequently are difficult to interpret absolutely. No response to ageing at 25°C is to be seen in γ_C ; at 40° and 60°C, however, there is a distinct increase in the critical surface tension. Qualitatively the polymer surface becomes less "styrene-like" and more "acrylic" in nature as it ages at these temperatures. Moreover, the rate of change increases with temperature, inferring the existence of a kinetic process. It is not possible to elaborate on the causes of this change, although thermally-initiated degradation or the diffusion (migration) of acrylic homopolymer moieties may be cited as mechanisms which could lead to the observations. It is beyond doubt, however, that this relatively simple experimental approach demonstrates a systematic change in the kind of surface which a coating such as this would present to any inter-acting (potentially penetrating) liquid or vapour. Assuming that the γ_C rise indicates an increasing polarity of the polymer surface, its wettability—for example—and hence its moisture resistance might also be expected to change.

S/MMA/MAA + BBP: The data in Table 2 for this composition show no significant time dependence at any of the three ageing temperatures. The result confirms earlier indications of the good compatibility between polymer and plasticiser and shows that this compatibility extends to relatively high temperatures. (It is hoped that a fuller discussion of this matter, will be presented in a future publication). Further, it is noted that in the presence of BBP the time dependent increase of γ_C for the host polymer is suppressed. It is possible that the plasticiser acts as a mild antioxidant, though there is no *a priori* reason to associate such an action with the BBP molecule. In view of the inferred compatibility between the liquid and the polymer components, however, it is also possible that the mobile fluid acts as a solvent for incompletely polymerised fragments in the copolymer mass. In this manner, exudation to the surface would be hindered or stopped; this argument appears more reasonable and suggests that the effect observed in Table 2 for *S/MMA/MAA* may be due to the presence of such moieties in the copolymer sample.

Conclusions

A simple and relatively rapid method has been developed for the measurement of critical surface tension and its temperature dependence in complex polymer formulations used as film-formers. The method is based on an adaptation of the thermal gradient bar, an instrument familiar in coatings technology.

Critical surface tension data have been shown useful in detecting glass transition effects in coatings.

The compatibility of polymer/plasticiser combinations has been monitored successfully by surface tension data, over significant ranges of composition and temperature.

The present experimental approach is well suited for the measurement of ageing effects in surface coatings.

The described method should find a wide range of applications in practical work, representing a useful complement to such procedures as solubility parameter calculations in the evaluation of physical interactions among the components of a coatings system. Its use as a guide to property optimisation in coatings, is indicated.

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The microanalysis of copper oxide based marine antifouling paints in the scanning electron microscope

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Summary

The scanning electron microscope with X-ray microanalysis is proving to be a valuable tool with which to follow compositional changes occurring in antifouling paints during service. It is recognised, however, that such paint is far from being the microscopically homogeneous type of material to which the theory of quantitative X-ray microanalysis strictly applies. Consideration has been given, therefore, to the interaction of an electron beam with such a sample and the subsequent emission of X-rays. It is shown that a low electron energy (5 kV) favours good microscopy, but confines X-ray analysis to a dangerously thin surface layer, having regard

to the difficulties of preparing sections with undisturbed and truly representative surfaces. At an electron energy of 20 kV, which gives inferior microscopy, the analysed depth varies from about 0.5 to 3 μm and is correspondingly less sensitive to any non-representative surface layer on the prepared section. Normal analytical procedure has given satisfactory results with these paints, but for paints containing other solid material in addition to the copper oxide, errors due to X-ray absorption losses may make it advisable to calibrate with paints of known composition.

Keywords

Types and classes of coatings and allied products
antifouling coating

Raw materials for coatings
binders (resins, etc.)
copper oxide

Processes and methods primarily associated with analysis, measurement or testing

electron microscopy
X-ray analysis

manufacturing or synthesis
leaching

La microanalyse par microscope électronique à balayage des peintures "antifouling" à base de l'oxyde de cuivre

Résumé

Le microscope électronique à balayage en combinaison avec la microanalyse par rayons X se montre utile pour étudier les changements de composition qui se produisent au sein des peintures "anti-fouling" pendant leur vie effective. On reconnaît, cependant, qu'une telle peinture est loin d'être une substance homogène au point de vue microscopique, et à laquelle la théorie de microanalyse par rayons X s'applique strictement. Par conséquent on a étudié l'interaction d'un faisceau d'électrons et d'un échantillon d'une telle peinture et l'émission des rayons X qui en résulte. On démontre que les électrons de faible énergie (5kV) favorisent la microscopie, mais qu'ils bornent l'analyse par rayons X à une trop mince couche superficielle, compte tenu des difficultés en ce

qui concerne la préparation des lames ayant les surfaces tout à fait caractéristiques et inaltérées. Les électrons d'une énergie de 20kV nuisent à la microscopie, et la profondeur susceptible à l'analyse se varie entre 0,5 μm à peu près et 3 μm , et par conséquent elle est moins sensible à toute couche superficielle non caractéristique qui se trouve sur la lame élaborée. Les méthodes d'analyse normales ont donné des résultats convenables dans le cas de ces peintures, mais à l'égard des peintures contenant d'autre matière solide aussi bien que l'oxyde de cuivre, les erreurs provoquées par l'absorption de rayons X rendent prudent la calibration du système au moyen des peintures de composition connue.

Die Mikroanalyse von Schiffsantifoulingfarben auf Kupferoxidbasis mittels Abtastelektronenmikroskop

Zusammenfassung

Das Abtastelektronenmikroskop mit Röntgen-Mikroanalyse bewährt sich als ein wertvolles Werkzeug zur Verfolgung von in Antifoulingfarben während ihrer Dienstzeit vor sich gehender Veränderungen in ihrer Zusammensetzung. Man ist sich indessen bewusst, dass solche Farbe weit davon entfernt ist, ein mikroskopisch homogener Materialtyp zu sein, für welchen die Theorie quantitativer Röntgen-Mikroanalyse strikt anwendbar ist. Der Reaktion zwischen einem Elektronenstrahl mit solch einem Muster und der nachfolgenden Emission von Röntgenstrahlen wurde daher Beachtung geschenkt.

Es wird gezeigt, dass niedrige Elektronenenergie (5 KV) gute Mikroskopie begünstigt, aber Röntgenstrahlenanalyse auf eine

gefährlich dünne Oberflächenschicht beschränkt, wenn man bedenkt, wie schwierig es ist, Schnitte mit ungestörten und wahrhaft typischen Oberflächen zu präparieren. Bei einer Elektronenenergie von 20 KV, die minderwertige Mikroskopieresultate ergibt, schwankt die analysierte Tiefe zwischen etwa 0.5 bis 3 μm und ist entsprechend weniger empfindlich bei jedweder untypischen Oberflächenschicht auf dem präparierten Schnitt. Normales analytisches Arbeiten ergab mit diesen Farben befriedigende Resultate, für Farben aber, die andere Festkörper ausser dem Kupferoxid enthielten, kann es, als Folge von Röntgenstrahlenabsorptionsverlusten, ratsam sein, mit Farben bekannter Zusammensetzung zu kalibrieren.

Introduction

Refs. 1-7, 13

An economic factor of great importance in marine transportation is the length of time for which a ship can serve before hull fouling, leading to loss of efficiency, necessitates costly dry-docking, cleaning and repainting. This time is primarily dependent on the performance of the antifouling paint employed, and a great deal of effort is now going into the

assessment of present day antifouling paints and the development of better ones.

The primary functions of an antifouling coating are to provide a reservoir of one or more substances toxic to the marine organisms causing the fouling, and to release the toxicants in such a manner as to ensure low but protective concentrations at the paint surface over an extended period of time. As the active material is dissolved in the sea water

and lost from the paint, that remaining in the film may change not only in concentration, but also in distribution through the film. The study of such compositional changes calls, therefore, for microanalysis such as may be carried out in an electron probe microanalyser or better still a scanning electron microscope (SEM) with X-ray analytical facilities. The SEM has been used to study antifouling paints^{1,2,3} but this was largely microscopy of the surfaces and of the fouling organisms. The instrument has also been applied to the study of other coatings,^{4,5,6,7} again largely on the microscopy of the surfaces. Analytical work on paints has already been carried out in electron probe microanalysers (mainly) in connection with works of art but, as pointed out in Ref. 13, the inhomogeneous nature of paints places a severe limitation on the possibility of accurate quantitative analysis. Additionally, the organic binding material is likely to be badly damaged by the beam intensities necessary for the more conventional type of electron probe analysis using crystal X-ray spectrometers. These factors have, undoubtedly, limited the application of electron probe analysis in paint investigations. However, with the advent of improved semi-conductor detectors for energy-dispersive X-ray analysis, analysis has become possible at the much lower electron beam intensities sufficient for scanning electron microscopy. The inherent difficulty with analytical accuracy remains, but in the author's laboratories large numbers of test panels are now examined in this way with sufficient accuracy for the work in hand.

In the normal application of electron-excited X-ray emission to quantitative microanalysis, the basic assumption is made that the sample is homogeneous over the analysed volume. This usually extends over a few cubic microns at the point of impact of the electron beam. Such an assumption cannot be made with paints and it is, therefore, impossible to obtain accurate results by the application of the well developed and widely employed correction procedures for the elimination of errors due to inter-element and other effects. Quantitative results must be expected to be of a rather approximate nature but, nevertheless, it is very valuable to be able numerically to characterise paint films for toxicant content and to follow changes occurring during service. It is, of course, desirable to go further and obtain some ideas on the best choice of examination conditions and how realistic and accurate such analytical results may be. It is the purpose of this paper to consider the problem arising in the analysis of paints based on cuprous oxide; a further publication will refer to the still greater problem with more recent paints based on other toxicants that can be present in a much coarser particulate form.

The preparation of paint specimens for examination and some of their characteristics

The paints are usually tested on flat fibre glass substrates which may readily be attached to a ship's hull or a test raft for exposure. In practice, antifouling paints are supplied for use over specified undercoats. These are employed also on the test panels, so that several layers are usually present. It is important that films should be of uniform thickness and to this end they will have been applied by a spreading technique rather than brushing or spraying. A representative strip is sawn from each test panel and set perpendicularly in a block of suitable polymerisable mountant. The choice of this mountant is important in that it must not swell or otherwise disrupt the paint layer before polymerisation occurs. The surface of the block is carefully worked back to provide a surface suitably smooth for examination using a series of progressively finer abrasive papers under flowing water, terminating with 600 grade. This is not easy because of the

considerable hardness difference between the organic binder of the paint and the incorporated particulate matter. The particles can be lost from the surface and the binder deformed and smeared. It is often advisable to carry out the surface preparation at low temperature using liquid nitrogen cooling. This helps to keep the polymer below its glass transition point and thus minimises deformation. It is of no advantage to finish with finer diamond abrasives, such as are used in metallurgy; indeed, the liquid material in some of these preparations can soften and damage the polymeric constituent of the paint film. The surfaced specimen is usually coated with a layer of carbon to make it conducting before examination in the microscope.

Antifouling paint based on cuprous oxide is the type most commonly employed hitherto and it is still widely used. It consists of a heavy loading of cuprous oxide in a medium fairly permeable to water, so that the chemical may be leached out. Such a paint is illustrated in section in Fig. 4 and in Fig. 5 (upper pair of micrographs). The paint contained 80 per cent by weight cuprous oxide in a medium mainly of vinyl polymer, which contained 66 per cent carbon, 8 per cent hydrogen and 25 per cent chlorine.

The surface of the prepared specimen is reasonably flat and there is little topographical detail. The copper oxide is seen clearly by reason of its greater electron back-scattering power. The upper pair of micrographs shown in Fig. 5 are of a paint film that had suffered no exposure and are of the same area of specimen taken at two different beam voltages (20 kV, the setting used when good X-ray excitation is required for analysis, and 5 kV at which better microscopy is possible), the copper oxide particles being more clearly revealed by reason of the reduced diffusion of the lower energy electrons. The lower pair of micrographs in Fig. 5 are of a film that had been exposed for 179 days on a ship's hull and show that the cuprous oxide particles remaining in the bulk of the film are not characteristically changed. The copper oxide has a particle size of about 0.3 μm , but there is a tail to the distribution, running up to about 1 μm . There is considerable agglomeration which gives rise to tight clusters of particles in the size region 1 to 3 μm . At the higher beam voltage it is frequently difficult to discern that these are clusters and not single particles.

The compositional changes that occur in antifouling paints during service are for the most part a function of their position through the paint film. That is to say, the composition at a given depth tends to be constant over a prepared uniform paint film. This gives an opportunity to overcome the difficulty of inhomogeneity, at least in part, by considering average composition along lines parallel to the paint surface.

Microanalysis and the problems

Because, in principle, the composition of a well prepared paint film is constant at a given depth below the surface, it becomes possible to characterise the composition at that depth by the technique of line scanning in the electron probing instrument. Line scans are carried out parallel to the paint surface, and at a number of positions through the film as indicated in Fig. 3, where the size and spacing of the individual toxicant particles are small compared with the length of line. The average intensities of characteristic X-rays emitted under these conditions are compared with those emitted under the same conditions from suitable standards, and from the results, concentration profiles through the thickness can be obtained.

In such a case as this, where the sample volume excited at any one instant is comparable in size with the structural

detail, the usual correction procedures cannot be applied, as already stated, and results will be subject to error. In what follows an attempt is made to gain insight as to the accuracy of the results.

It is hardly feasible, and would not be profitable, to consider rigorously the intensity of X-rays emitted from the point of impact of the electron beam on such a heterogeneous sample, but in seeking a better appreciation of the analytical problem it is helpful to consider the emission in some simple cases. These are:

- (i) Pure cuprous oxide (Cu_2O).
- (ii) Binder containing cuprous oxide evenly distributed at a concentration low enough to have only a small effect on the behaviour of the electrons.
- (iii) Pure cuprous oxide with a thin layer of binder over it.

For electrons of 20 kV energy, this may be done along the lines originally put forward by Castaing¹⁴ who made use of a depth distribution of generated X-ray intensity $\phi(\rho z)$, the depth being expressed as ρz , the mass penetration of the electron beam to the depth z . This depth distribution has been found experimentally for various elements and electron beam energies. Brown¹⁵ has determined it for copper at an electron energy of 18.2 kV which is reasonably close to the 20 kV under consideration. He had worked with the electron beam inclined at 30° to the normal of the sample surface, different from the 15° employed in the present work, but his data were adaptable to the author's purpose by applying the factor $\sec 30^\circ / \sec 15^\circ$ to the ρz scale.

The X-ray intensity generated at a given depth in a sample is attenuated by absorption along the path out. Formally the intensity emerging may be written as:

$$dI = \phi(\rho z) \exp\left(-\frac{\mu}{\rho} \rho z \csc \psi\right) d(\rho z)$$

where μ/ρ is the X-ray mass absorption coefficient and ψ is the take-off angle of the X-rays relative to the sample surface.

To obtain the approximate distribution of emergent X-ray intensity as a function of depth of generation, Brown's distribution was divided into eighteen equal increments of ρz and the component of intensity emerging from each was deduced from the above expression for a take-off angle of 15° , for specimens of Cu_2O and paint medium. Calculations were also made for cases where first one, then two, then three, and so on up to seventeen increments of mass thickness were assumed to be paint medium overlying Cu_2O .

Fig. 1 shows the distribution in depth of the emitted Cu K X-rays for samples of Cu_2O and paint binder with a very small copper content. Taking as a measure of the depth of analysis, the depth from which the emergent radiation intensity is less than the maximum by a factor of $1/e$, the depths of analysis in the oxide and the binder are seen to be $0.55 \mu\text{m}$ and $2.6 \mu\text{m}$ respectively.

For the third case, that of a sample consisting of Cu_2O with an overlayer of paint medium, it is convenient to consider integrated total emergent intensities:—

$$I = \int_0^\infty \phi(\rho z) \exp\left(-\frac{\mu}{\rho} \rho z \csc \psi\right) d(\rho z)$$

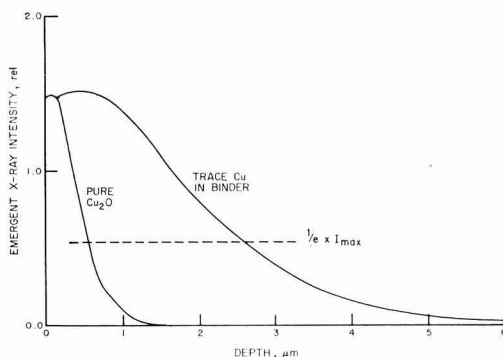


Fig. 1. Depth distribution of emergent X-ray intensity

An adequate approximation to this was taken as the sum of the component intensities from the 18 finite intervals of depth. To simulate the copper-free overlayer, Brown's intensity function was set equal to zero over the appropriate interval. Total intensities obtained in this way were expressed as ratios against the case of no overlayer, to give the solid line relationship of Fig. 2. This shows that there could be an intensity loss of about 20 per cent for an oxide specimen with an overlay of medium $0.4 \mu\text{m}$ thick.

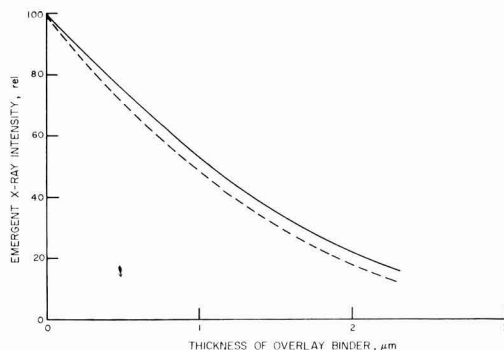


Fig. 2. Effect of layer of binder over Cu_2O on emergent X-ray intensity

The treatment so far has taken no account of the atomic number effects that are significant in accurate electron probe analysis. This was considered after the manner of Duncumb and Reed.¹⁶ With large changes in atomic number the mass penetration of the electron beam will not be quite the same, and there will similarly be differences in the electron losses by back scattering. The influence of these effects on the observed X-ray intensity may be expressed by a factor

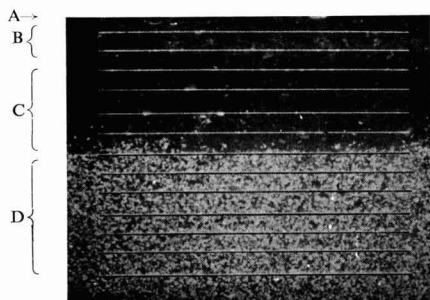
$$R/S$$

where R is a back scatter coefficient that would be unity for no back scatter and S is the electron stopping power discussed further below.

Evaluation of this factor for Cu_2O and the paint binder with a small copper content, using Duncumb and Reed's data, showed that on changing from a sample of oxide to one of the binder, atomic number effects would depress the expected X ray intensity by about 20 per cent. This would act progressively with increasing thickness of binder overlay and in

Fig. 2 a more appropriate relationship would be something like the dotted line. Thus an overlay of thickness $0.4 \mu\text{m}$ would reduce the observed X-ray intensity by a little more than 20 per cent.

This treatment of composite samples is open to criticism in that the distribution of electron energies and trajectories within the sample will not be strictly unchanged on substituting a given mass of cuprous oxide at the surface by a similar mass of binder, although consideration of the atomic number effect will help to cover the point. A more satisfactory treatment would involve a Monte Carlo simulation procedure and a massive computing exercise as described by Kyser and Murata.¹⁷ Bishop and Poole¹⁸ published some less rigorous information of this kind intended for general application to film thickness measurements, but this did not take account of atomic number effects. However, in the present instance of substrate emission through thin surface layers of low atomic number material, the errors with the simple treatment are unlikely to be large.



The superimposed lines above show the positions at which analysis was carried out

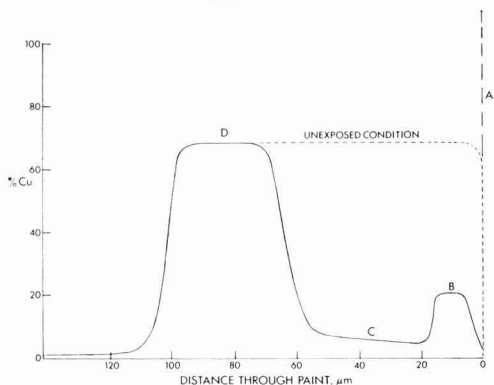


Fig. 3. Concentration profile of copper in exposed paint film: A, outer surface; B, outer copper-rich layer; C, copper depleted region; D, intact poison

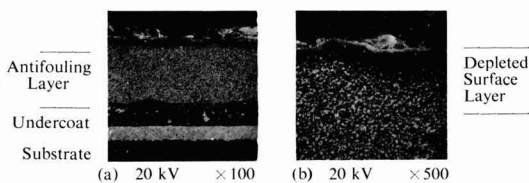


Fig. 4. Scanning electron micrographs of section through antifouling paint film

The case of a thin layer of paint medium over a substrate of cuprous oxide is of relevance in the study of real paints in that it gives insight into the consequences, should poor specimen preparation technique give rise to a surface layer enriched in paint medium and unrepresentative of the body of the paint film.

Analysis for copper is normally carried out using the K radiation, which for efficient excitation requires a beam voltage of 20 kV or more; but it would be possible with an electron beam energy of 5 kV, a setting giving better microscopy of the sections. This could be done by observing the Cu L radiation to which the solid state detector is adequately sensitive. It is, unfortunately, not possible to repeat for the lower voltage the foregoing considerations of emitted X-ray intensity, because there is no corresponding published basic data on X-ray emission; some rough ideas can, nevertheless, be obtained.

At the higher voltage, absorption losses were not large so that analysed depth was determined more by the range of the incident electrons, that is, by the electron stopping power of the sample, to which brief mention has already been made above. Consideration of the relative electron stopping powers of the sample at the two voltages will, therefore, set an upper limit to the analysed depth at the lower voltage. Electron stopping power was evaluated after the manner of Duncumb and Reed.¹⁶

When energetic electrons interact with matter, some of the energy is lost in inner shell ionisations which subsequently give rise to the X-ray emissions on which electron-probe microanalysis is based. A large part of the energy loss is, however, associated with the ejection of outer electrons of much lower ionisation potential. The pattern of energy loss changes with atomic number, and in microanalysis account is taken of this effect by considering electron stopping power defined as:

$$S = \frac{1}{\rho} \frac{E}{X}$$

where ρ is density

E is electron energy

X is distance along electron path.

Defined in this way, electron stopping power for a given element is approximately constant regardless of physical or chemical state and for multi-element samples:

$$S = \sum_i C_i S_i$$

where S_i is the electron stopping power of the i th element and C_i is its fractional concentration.

The most suitable expression for stopping power is that given by Bethe.^{19,20}

$$S = \text{const.} \frac{Z}{A} \frac{1}{E} \ln \frac{1.166E}{J}$$

He derived it originally for the stopping power of protons and other positive ions by hydrogen atoms. In applying it to the stopping of electrons by other elements J has to become a mean ionisation potential.

Duncumb and Reed, working backwards from electron probe analysis of known binary samples, obtained improved values of J . Using their data, the values found for the stopping power of Cu_2O and the paint binder, for electrons of energies 5 and 20 kV, are as in Table 1, in which the figures are actually

ρS , so as to relate to distance penetration rather than mass penetration.

Table 1
Relative electron stopping powers

Material	Relative stopping power (ρS)	
	5 kV electrons	20 kV electrons
Paint binder	50	17
Cu ₂ O	160	60

It will be seen that the stopping power of the binder at the lower voltage is about three times that at the higher voltage, and that in both cases the stopping power of the oxide is about three times that of the binder. Thus, if the limitation is mainly due to the stopping of the exciting electrons, then from considerations above, the depth of analysis at the lower voltage will be about 0.2 μm in Cu₂O or 0.8 μm in the binder. Absorption data for Cu L radiation are not available, but the losses would be much greater than for the K radiation and substantial for the foregoing sample thicknesses. It may be said, therefore, that the depth of analysis would be less than 0.2 μ in Cu₂O and less than 0.8 μm in binder. Furthermore, judging from the increased electron stopping power, a little over 0.1 μm of binder would reduce emergent X-ray intensity by 20 per cent. Thus it will be seen that the problem of producing a representative specimen surface suitable for analytical purposes at low beam voltage would be rather exacting.

Given good samples of surface composition representative of the bulk, there is still likely to be more error involved in analysis at low electron energies, as the analysis is confined more closely to the surface. This follows because the average X-ray intensity observed would be proportional to the percentage area of cuprous oxide in the surface. It is a well established fact of stereology²¹ that in a section through a heterogeneous material, the percentage area occupied by a disperse phase is equal to its volume percentage within the body. Thus for 80 per cent by weight Cu₂O in a resin, allowing for density difference, it would be expected that only 42 per cent of the specimen surface would be Cu₂O, and a copper analysis correspondingly lower than this, in the region of 38 per cent would be obtained.

The physical picture in depth of the region analysed in line scanning mode with a beam energy of 20 kV may be gathered

Note that the X-rays will generally leave the surface with a shorter path length than that required for 20% absorption in pure Cu₂O, and since the medium is much less absorbing the losses will be much less than 20%.

Paint surface

1 μm [

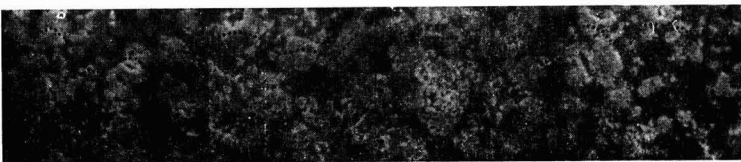


Fig. 6. Analysed depth in a representative region with an electron accelerating potential of 20 kV
..... represents approximate depth of penetration of electron beam

from normal sectional micrographs such as Fig. 5. Regions of such a paint film, away from the surface, may reasonably be assumed isotropic, and the micrographs of sections will, therefore, equally typify the chemical distribution in a plane perpendicular to the specimen surface, *ie* the plane of incidence of the electron beam. Fig. 6 is a portion of a micrograph at higher magnification, taken to represent distribution in depth, and on it a rough indication is made of the depth of analysis as the beam scans along the surface. Drawn to scale in the X-ray take-off direction is the length of path in Cu₂O required to reduce the intensity of Cu K _{α} radiation by 20 per cent. It will be seen that the dominant effect in determining analysed depth is the penetration of the electron beam.

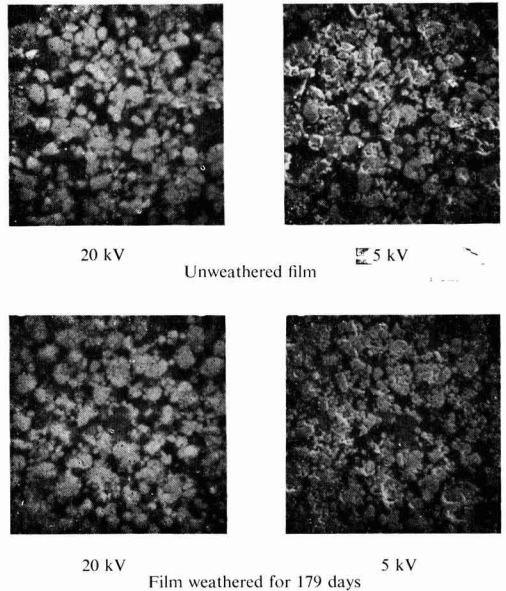


Fig. 5. Scanning electron micrographs of sections of unweathered and weathered paint films

Although the analysed depth cannot much exceed 2.5 μm this is substantially larger than the primary particle size of the

Path length for 20% X-Ray absorption in pure Cu₂O



Paint surface

- 1 μm
- 2 μm
- 3 μm

cuprous oxide. If the copper oxide particles are not too badly agglomerated, it seems possible that for reduced concentrations of the substance the analysed depth might tend to increase in a manner to compensate to some extent for the expected fall of observed X-ray intensity. The availability of simple copper oxide paints was unfortunately limited. In specially made paints of lower than usual loading, flocculation and separation of the oxide proved very troublesome.

Paints of lower copper content were available, but these contained other, for the most part more finely divided, particulate matter, that would be expected to alter the electron penetration and the X-ray absorption losses. Results on three out of five such paints are as good as those on the simple paints.

Test results and applications

Although detailed consideration of this type of analysis stresses the far from ideal nature of the samples, and does not present a good prospect for analytical accuracy, experience has been encouraging. Results obtained on some unweathered paints of known composition are presented in Table 2.

Table 2
Electron microprobe analysis results on copper-rich antifouling paints

Paint	Copper content %w		
	Stated Cu content, %w	Result at 20 kV beam voltage	Result at 5 kV beam voltage
A	71	70	55
B	72	68	
C	65	60	
D*	57	55	
E*	46	42	
F†	60	58	
G†	60	51	
H*	53	40	

* also contained a well distributed tin compound together with finely divided mineral matter.

† also contained large particles of a tin compound together with finely divided mineral matter. The copper result has been corrected slightly by a procedure to be discussed in a further paper.

Paint A is the simple copper oxide paint to which this paper in great part refers. The result obtained at reduced beam energy with the Cu L radiation is lower, as would be expected from the reduction of depth of analysis and the greater sensitivity to non-representative surface.

As already mentioned, it proved impossible to obtain satisfactory behaviour in simple copper oxide paints of low oxide content (below about 50 per cent). Paints A, B and C covering the range of stable dispersions all gave satisfactory results.

This type of line scan analysis is proving very effective in the exploration of element distributions through paint films, and the changes in such distribution during service. As shown in Fig. 3 the line is arranged parallel to the surface, and is

placed at various depths as noted on a graticule mounted over the viewing screen of the electron microscope. (This graticule is actually two similar graticules mounted with a spacer, so as to control parallax errors.)

During service, the paint referred to for the most part in this report developed a copper-depleted layer extending inwards from the outer surface; and indeed this can be seen in Fig. 4a. The copper concentration in this region fell generally to about five per cent, but in places, regions of intermediate copper content developed immediately adjacent to the outer surface (found to be due to insoluble copper salts). These features are shown in Fig. 3. The concentration of the copper in the inner part of the film remained constant, but as the sea-exposure time increased the depletion zone increased in thickness. At a time when fouling had set in on the paint surface, the depleted zone had attained a thickness of about 70 μm . A substantial part of the original copper content still remained within the film, but its leaching rate through the outer depleted layer was apparently reduced to the point of ineffectiveness. Different behaviours have been observed with other paints.

Conclusions

The combination of semi-conductor X-ray detection carried out in a scanning electron microscope makes possible routine X-ray microanalysis of copper-based antifouling paint films, satisfactory cross-sectional specimens for analysis being prepared by wet grinding at low temperature.

Detailed consideration of the interaction of the electron beam with such samples indicates that under conditions suitable for analysis with Cu K_{α} radiation the analysed depth is about 3 μm .

Line-average X-ray intensities for Cu, expressed as ratios of those for the pure element, give the approximate copper contents in acceptably good agreement with known bulk concentrations. This holds for fairly high copper contents, but has not been verified for lower contents.

Although the accuracy of results at low copper contents is unknown, the method facilitates valuable studies of toxicant distribution in paint films, and of changes in distribution with time.

Limited work on more complex paints continues to show satisfactory agreement between known copper contents, and results by this simple approach to analysis. This encourages the extension of the investigations to antifouling paints more generally, including other chemical elements, and a further paper is in preparation.

It is a pleasure to acknowledge the help in this work of D. Park who carried out most of the microanalysis and D. W. Singleton who prepared many of the paint specimens.

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Next month's issue

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

New methods of determining the throwing power of ED paints by *H. Hönig*

The painting of Inter-city passenger trains by *F. D. Timmins*

Disposal methods for hazardous wastes by *R. A. Fish*

Electrical aspects of radiation curing by *W. C. Hankins*

2D colour diagram based on sensitivity functions of cone vision (*Short Communication*) by *A. F. Murphy*

Non-conventional anti-corrosive primers for steel*

By D. E. A. Williams-Wynn

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Summary

Two sets of experimental primer paints, incorporating active pigments not commonly used in primers for steel, have been exposed in Durban for about two years, and have also been subjected to salt spray testing. Commercial primer paints were exposed under similar conditions to act as controls.

Some of the experimental paints have performed very well, fre-

quently surpassing zinc chromate or red lead primers, although the zinc rich primers were superior. The results have shown that the incorporation of iron oxide with the active pigments in the experimental paints has greatly improved their performance on exterior exposure in Durban. A further notable observation is the lack of correlation between salt spray testing and exterior exposure for predicting primer performance.

Keywords

Types and classes of coatings and allied products

anticorrosive coating

Types and classes of structures or surfaces to be coated

steel

Properties, characteristics and conditions primarily associated with

the environment

exterior exposure

Processes and methods primarily associated with analysis, measurement or testing

salt spray test

Raw materials—pigments prime pigments and dyes

lead silico chromate

red lead

chrome fluoride

chemically active pigments

zinc molybdate

zinc phosphate

zinc chromate

zinc dust

paint additives

barium metaborate

Peintures primaires de composition exceptionnelle pour acier

Résumé

Deux séries de peintures primaires expérimentales à base de pigments actifs, que l'on n'utilise pas usuellement en primaires pour acier, ont été exposées à Durban pendant deux ans à peu près, et elles ont été soumises à l'essai au brouillard salin. Des peintures primaires de commerce ont été également exposées en tant que témoins.

Certaines des peintures expérimentales se sont comportées très bien, souvent dépassant les primaires à base de chromate de zinc

ou de minium de plomb, bien que les primaires à base de fortes quantités de poudre de zinc fussent supérieures. Les résultats ont démontré que la résistance aux intempéries à Durban des peintures expérimentales a été fortement augmentée où l'oxyde de fer a été incorporé avec les pigments actifs. Une autre observation remarquable c'est le manque de corrélation qui existe entre l'essai au brouillard salin et la résistance aux intempéries au point de vue de la prédiction du rendement des peintures primaires.

Unkonventionelle und antikorrosive Primer für Stahl

Zusammenfassung

Zwei Gruppen von experimentellen Primerfarben, enthaltend aktive Pigmente, welche normalerweise nicht in Primern für Eisen und Stahl benutzt werden, wurden in Durban etwa zwei Jahre lang bewittert und ausserdem dem Salzsprühnebeltest ausgesetzt. Als Kontrollen wurden handelsübliche Primerfarben unter gleichen Bedingungen der Witterung ausgesetzt.

Einige der Versuchsfarben verhielten sich sehr gut, häufig

besser als Zinkchromat- oder Bleimennige-Primer, allerdings waren zinkstaubreiche Primer überlegen. Die Ergebnisse erwiesen, dass die Einverleibung in die Prüffarben von Eisenoxid zusammen mit aktiven Pigmenten deren Verhalten bei Bewitterung in Durban wesentlich verbesserte. Weiterhin ist die Beobachtung bemerkenswert, dass zwischen der Salzsprühnebelprüfung und der Bewitterung keine Korrelation besteht, um das Verhalten der Primer vorauszusagen.

Introduction

Refs. 1-61

Lead pigments have been and are extensively used in anti-corrosive primers for steel; new priming materials, in particular the zinc rich coatings, have been shown to give superior effects, especially in marine or industrially polluted environments, but they are successful only if the surface preparation before the application of the primer is of a particularly high order. This is not always possible to achieve, and makes these speciality coatings of limited interest in

maintenance painting. Lead based paints, however, are relatively tolerant of surface contamination and continue to enjoy wide use, but the toxicity of lead has prompted a search for alternative, equally effective materials for use in anti-corrosive coatings. The problems of corrosion, toxicity and the environment were highlighted in an editorial published recently¹.

Numerous articles have appeared within the last few years dealing with primer performance and metal protection. Some of these are of a general nature, especially concerned with

*Extended version of the paper presented at the Sixth National Symposium held jointly by the South African Division of OCCA and CSIR at Port Elizabeth on 8 and 9 October 1976.

accelerated testing and predicting primer performance²⁻⁴, and others are concerned with preconstruction metal protection both from corrosion and mechanical damage⁵⁻⁷. The economic aspects of corrosion protection have also been considered⁸.

Red lead and other lead pigments⁹⁻¹³ and metallic lead powder¹⁴⁻¹⁵, as well as other anti-corrosive coating systems¹⁶⁻²³, have received attention. Zinc rich coatings are a special case; Brushwell has reviewed their use²⁴ and other papers have appeared²⁵⁻²⁷, but as coatings in marine situations they seem to have a particular advantage²⁸. The problems of protecting steel in marine and other underwater environments has been the subject of numerous reports²⁹⁻³⁷, and many reports have appeared dealing with steel protection in general³⁸⁻⁵³. Water based primers are also receiving attention⁵⁴⁻⁵⁶ but, whilst these are of considerable potential interest, the solvent systems are still the most important.

The problems involved in the selection of suitable primers and paints for steelwork have been made more difficult with the introduction of a multiplicity of priming systems and the claims and counterclaims of manufacturers and suppliers. The economic aspects of corrosion protection have to be taken into account⁸ and the service life and maximum service temperatures of the various classes of paints have to be considered before a proper assessment of cost/effectiveness can be made. Architects and engineers are faced with ever increasing problems in specifying paint systems, and specifications and codes of practice have to be carefully considered in every detail⁵⁷.

Work, commenced at the SA Paint Research Institute in 1973, has been continued in this department, and the results quoted in this paper are either from SAPRI publications⁵⁸⁻⁶⁰, or recent evaluations of samples after exposure in Durban for two years. Durban is ideally situated for exposure testing of this kind, being classed as having a marine-industrial atmosphere⁶¹, and of 22 test sites around the world Durban was ranked fourth for corrosion of steel. Unprotected 1 to 1.5mm thick mild steel plates corrode to complete disintegration in less than two years in Durban.

Experimental

Results of preliminary investigations

Refs. 2, 3, 58, 60

Nine pigments or pigment combinations were incorporated into a "basic formula" anti-corrosive coating and evaluated by exposure to salt spray and natural weathering. The pigments included zinc molybdate, zinc phosphate, modified barium metaborate, chrome fluoride, and each of these in a 1:1 blend with iron oxide. In addition, a formulation including basic lead silico-chromate was used and compared with two commercial red lead paints to SABS 312-1951, a commercial zinc chromate to SABS 679-1972 and a marine zinc chromate paint. Two additional primer paints, a chlorinated rubber zinc rich primer and an inorganic zinc rich primer, were added at a later stage, and their exposure ran concurrently with the other paint coatings under test. Details of the experimental paint systems have been reported in earlier publications^{58,60}—briefly the compositions and application were as follows:

Basic formula

The active pigments or pigment blends were substituted on a mass basis which meant that the pigment volume concentration of the paints was not consistent.

	Parts by weight
Main pigment (or pigment blend)	133
Titanium dioxide, RCR-2	46
Aluminium distearate	1
Bentone 38	0.7
Alkyd P. 470	87
Drier blend	4.5
Exkin	0.7
White spirit (approximate quantity to adjust viscosity)	60

The aged paints were applied to three well abraded, solvent cleaned, mild steel panels such that the dry film thickness was 35 ± 3 micrometres. After 7 days of drying, half of the face of each panel was overcoated by brush with a good quality high gloss enamel, which was allowed to dry for a further 7 days before exposures were commenced. One set of panels was exposed to the Durban atmosphere on the roof of the SA Paint Research (now Applied Chemistry) building, and another set was subjected to the ASTM B117-64 salt spray test. Each coating was scored through to the metal with an X mark before exposure.

The only experimental primer to show up well after 1000 hours of salt spray was that in which the chrome fluoride plus iron oxide blend was the active pigment. On natural exposure for 270 days three paints, namely, those containing basic lead silico-chromate, zinc phosphate plus iron oxide, and chrome fluoride plus iron oxide were performing well when a more comprehensive study was begun. Nevertheless these results, although open to criticism because of the substitution of pigments or pigment combinations on an equivalent mass basis in a basic formula, indicated some promising performances, often better than commercial red lead or zinc chromate primers exposed under the same conditions. These results are summarised in Table 1.

Table 1
Results of preliminary investigation exposure tests
on anti-corrosive primers;
unprotected primers only

Pigment/primer	Exposure	
	270 days exterior	1000 hours salt spray
E. Zinc molybdate	poor	poor
F. Zinc phosphate	fair	poor
G. Barium metaborate	poor	poor
H. Chrome fluoride	fair	poor
I. Basic lead silico-chromate	good	fair
J. Zinc molybdate/iron oxide	fair	poor
K. Zinc phosphate/iron oxide	good	fair
L. Barium metaborate/iron oxide	poor	poor
M. Chrome fluoride/iron oxide	good	good
N. Red lead	fair	fair
O. Zinc chromate	fair	poor
R. Chlorinated rubber zinc rich*	good	good
S. Inorganic zinc rich primer*	v. good	good

*The results for these primers are not strictly comparable with the others since, although they were exposed for the same total period, the exposures were carried out at a different time of year.

In a report submitted by the Scientific Adviser to the Greater London Council, it is claimed that their experience in England had revealed a fair correlation between a 7 months natural exposure of primers only, and the longer term anticipated performance of three-coat systems (primer,

undercoat, gloss finishing coat) employing these primers^{2,3}. On this basis the 270 day exterior exposure indicates that there are primers which have stood up very well. Further exposure was carried out for a total period of over two years, assessment being made at 500 days and 750 days. The results are shown in Tables 2 and 3 respectively.

Table 2
Results of exterior exposure tests on anti-corrosive primers;
preliminary investigation

Pigment/primer	Exposure 500 days :	
	Unprotected	Topcoated
E. Zinc molybdate	slight rust	good
F. Zinc phosphate	slight rust	good
G. Barium metaborate	rust	micro blisters
H. Chrome fluoride	rust	micro blisters
I. Basic lead silico-chromate	rust-blisters	micro blisters
J. Zinc molybdate-iron oxide	slight rust	good
K. Zinc phosphate-iron oxide	slight rust	good
L. Barium metaborate-iron oxide	slight rust	micro blisters
M. Chrome fluoride/iron oxide	micro blisters	good
N. Red lead	slight rust plus microblisters	micro blisters
O. Zinc chromate	slight rust	good
R. Chlorinated rubber zinc rich	spotty blemishes	good
S. Inorganic zinc rich primer	spotty blemishes	good, but adhesion of top coat poor.

Apart from the zinc rich primers, all unprotected primers showed some breakdown with rust spots or slight evidence of rust staining. A number of experimental three-coat paint systems have performed well, the primers in most cases utilising zinc molybdate, zinc phosphate or chrome fluoride as the active pigment.

Table 3
Results of exterior exposure tests on anti-corrosive primers;
preliminary investigation

	Exposure 750 days	
	Unprotected	Topcoated
E. Zinc molybdate	rust	good
F. Zinc phosphate	slight rust	good
G. Barium metaborate	rust	micro blisters
H. Chrome fluoride	rust/blisters	rust/blisters
I. Basic lead silico-chromate	rust/blisters	micro blisters
J. Zinc molybdate/iron oxide	rust	good
K. Zinc phosphate/iron oxide	rust	good
L. Barium metaborate/iron oxide	rust	micro blisters
M. Chrome fluoride/iron oxide	rust/blisters	slight rust
N. Red lead	rust/blisters	rust/blisters
O. Zinc chromate	slight rust	good
P. Red lead	rust	rust
Q. Marine zinc chromate	rust/blisters	blisters
R. Chlorinated rubber zinc rich	spotty blemishes	good
S. Inorganic zinc rich primer	spotty blemishes	good, but adhesion of topcoat poor

None of the unprotected experimental primer paint coats has withstood more than two years exposure without some form of breakdown and evidence of rust formation. Since these were not designed as single coat systems, the results for the topcoated panels are more realistic and here some excellent performances are evident.

In view of some justified criticisms of the experimental procedure, and since anti-corrosive primers appear to have a total pigment volume in the range of 35 per cent to 53 per cent, a second, more comprehensive experiment was undertaken to supplement the preliminary investigation.

Results of main experiment

Refs. 59 -

Details of the pigmentation, paint formulation and the preparation of the panels are given in SAPRI Technical No. 102⁵⁹. The paints were made up of nine pigments or pigment blends:

1. Modified barium metaborate
2. Barium metaborate/iron oxide
3. Zinc molybdate
4. Zinc molybdate/iron oxide
5. Zinc phosphate
6. Zinc phosphate/iron oxide
7. Zinc oxide
8. Zinc oxide/iron oxide
9. Chrome fluoride

which were incorporated into a vehicle consisting of 5 parts of alkyd plus 2 parts of raw linseed oil with appropriate amounts of driers and sufficient white spirit to give an acceptable application viscosity. The quantities of pigments were chosen so that, for each pigment or pigment blend, five paints were prepared varying in pigment volume concentration from 35 per cent to 55 per cent, in steps of 5 per cent. Because of the difficulty experienced in the uniform brush application of some of the primers due to their extremely poor hiding power (barium metaborate, zinc phosphate, chrome fluoride), application was made by doctor blade. The dry film thickness was 43 ± 5 micrometres.

Natural Exposure

Prepared panels consisting of primer coat only and scored through to the metal with an X mark were exposed in Durban commencing the exposure in January, 1974. Coating performance was evaluated from time to time with the following results shown in Tables 4, 5, 6 and 7.

Table 4
Natural (exterior) exposure, 29 days

Pigment	Pigment Volume Concentration				
	35%	40%	45%	50%	55%
Barium metaborate	-	-	-	-	†
Ba borate/iron oxide	-	-	-	-	†
Zinc molybdate	-	†	-	†	-
Zn moly./iron oxide	-	-	-	-	-
Zinc phosphate	-	-	-	-	†
Zn. phos./iron oxide	-	-	-	-	†
Zinc oxide	-	-	-	-	-
Zn oxide/iron oxide	-	-	-	†	†
Chrome fluoride	-	-	-	-	-

† = incipient breakdown

- = no breakdown, no rust, film intact.

29 days is an extremely short exterior exposure period, yet several of the priming paints showed signs of early breakdown. It is interesting to note that the majority of the breakdowns occurred in those coatings with a pigment volume concentration of 55 per cent. In one case, the zinc oxide/red oxide system, incipient breakdown also occurred at the 50 per cent PVC level. The coatings with zinc molybdate were out of step; early breakdown was noted at 40 per cent and 50 per cent PVC, but not at 35 per cent, 45 per cent, or 55 per cent.

Table 5
Natural (exterior) exposure, 100 days

Pigment	Pigment Volume Concentration				
	35%	40%	45%	50%	55%
Barium metaborate	-	-	-	†	††
Ba borate/iron oxide	-	-	-	†	†
Zinc molybdate	-	†	-	††	-
Zn moly./iron oxide	-	-	-	-	-
Zinc phosphate	†	-	-	-	††
Zn phos./iron oxide	-	-	-	†	†
Zinc oxide	-	-	-	-	-
Zn oxide/iron oxide	-	-	-	†	†
Chrome fluoride	-	-	-	-	-

† = incipient breakdown, signs of rust
 †† = rust spots other than at X mark
 - = no breakdown, film intact.

It is convenient to present the results in tabular form, as above, indicating which panels were showing signs of breakdown, but observations regarding the appearance or colour of the coatings may also be relevant. This information cannot be depicted in the table.

Table 6
Natural (exterior) exposure, 219 days

Pigment	Pigment Volume Concentration				
	35%	40%	45%	50%	55%
Barium metaborate	†††	†††	†††	†††	†††
Ba borate/iron oxide	††	††	††	†††	†††
Zinc molybdate	-	†	††	†††	†
Zn moly./iron oxide	†	†	†	*	†
Zinc phosphate	†	†	†	†	††
Zn phos./iron oxide	-	-	-	†	†
Zinc oxide	†	†	†	-	†
Zn oxide/iron oxide	-	-	-	†	†
Chrome fluoride	†	†	†	††	-

† = incipient breakdown, signs of rust
 †† = rust spots other than at X mark
 ††† = general discolouration and rust
 - = no breakdown, film intact
 * = panel damaged.

After more than seven months (January to August) of natural exposure several coatings were still unaffected and were performing well.

The zinc phosphate/iron oxide pigment blend and the zinc molybdate/iron oxide blend performed well at low pigment volume concentrations (35 to 45), and paints containing zinc oxide and iron oxide in combination have given excellent service over the whole range of PVC's studied.

Table 7
Natural (exterior) exposure, 500 days

Pigment	Pigment Volume Concentration				
	35%	40%	45%	50%	55%
Barium metaborate	†††	†††	†††	†††	††
Ba borate/iron oxide	††	††	††	†††	††
Zinc molybdate	†	††	††	†††	†
Zinc moly./iron oxide	†	†	†	††	†
Zinc phosphate	††	†	††	†	††
Zn phos./iron oxide	†	†	†	††	††
Zinc oxide	†††	††	†	†	††
Zn oxide/iron oxide	†	†	†	†	††
Chrome fluoride	††	††	††	††	-

† = incipient breakdown, signs of rust
 †† = rust spots other than at X mark
 ††† = general discolouration and rust
 - = no breakdown, film intact.

Salt Spray Evaluation

Refs. 62-64

Two sets of panels were prepared for salt spray. One set was not protected by a finishing top coat and the other was undercoated and topcoated. The results of these two evaluations are summarised in the Tables 8 and 9; all of the unprotected primer coats had failed after 460 hours of salt spray, whereas some of the complete paint systems were able to withstand 1750 hours of salt spray.

Table 8
Salt spray, 460 hours; primer only, no topcoat

Pigment	Pigment Volume Concentration				
	35%	40%	45%	50%	55%
Barium metaborate	††	†	†	††	†††
Ba borate/iron oxide	†††	†††	††	†	†
Zinc molybdate	†	†	†	†	†
Zn moly./iron oxide	††	††	††	††	††
Zinc phosphate	††	†	†	†	††
Zn phos./iron oxide	††	††	††	†††	†††
Zinc oxide	††	††	†	†	††
Zn oxide/iron oxide	†††	†††	††	†††	†††
Chrome fluoride	†††	†††	†††	††	-

††† = early breakdown, 72 hours
 †† = breakdown, 240 hours
 † = breakdown, 46 hours

After 460 hours of salt spray all of the remaining panels, shown † in table above, had deteriorated to such an extent that no further exposure was worthwhile. However, these are the formulations that have given the greatest resistance to salt spray and although they had broken down in under 500 hours, it must be remembered that they were not protected by a finishing topcoat. In fact, resistance to 250 hours of salt spray is generally regarded as satisfactory⁶².

Many of the paint systems had broken down after 500 hours of salt spray exposure, including all primers containing iron oxide. Nevertheless, there were a few overcoated primer systems, notably those made from barium metaborate and especially chrome fluoride, which withstood an extended salt spray exposure.

Table 9
Salt spray, 1750 hours; topcoated

Pigment	Pigment Volume Concentration				
	35%	40%	45%	50%	55%
Barium metaborate	††	†	†	††	†
Ba borate/iron oxide	†††	†††	†††	†††	†††
Zinc molybdate	††	††	†	††	††
Zn moly./iron oxide	†††	†††	†††	†††	†††
Zinc phosphate	††	††	††	††	††
Zn phos./iron oxide	†††	†††	†††	†††	†††
Zinc oxide	†††	†††	†††	†††	†††
Zn oxide/iron oxide	†††	†††	†††	†††	†††
Chrome fluoride	†	†	†	†	—

††† = early breakdown, 500 hours

†† = breakdown, 900 hours

† = breakdown, 1750 hours

Considerable differences were noted in the performance in salt spray tests between uncoated and complete finish systems. Of particular note is the poor performance of the uncoated chrome fluoride paints, whereas these primers in a complete paint system stood up extremely well to extended salt spray exposure. Unfortunately, the validity of the official ASTM salt spray test is questionable⁶²⁻⁶³—these observations tend to confirm the poor correlation to natural exposure, which Harrison attributes to the incorrect selection of solute in the salt fog⁶⁴. There appears to be no wholly satisfactory accelerated test which will obviate the need to evaluate paint systems in the environment in which they are to be used.

Conclusions

Refs. 64, 65

From the above results several observations can be made.

Firstly, several primer formulations incorporating non-conventional active pigment components have withstood exposure in Durban very well, frequently performing better than conventional commercial red lead and zinc chromate primers.

Secondly, of all the primers tested, only the zinc rich paints gave satisfactory performance without a topcoat. In fact, the adhesion of the topcoat to the inorganic zinc rich primer was poor and there was no evidence that this failure impaired the performance of this finish.

Thirdly, salt spray testing and natural exterior exposure did not rank the primer formulations in the same order. Evaluation by salt spray testing is acknowledged as having limited value, except in salt-laden or marine environments, and even for these conditions the official test solution is regarded as inappropriate⁶⁴.

Fourthly, there is no doubt that the incorporation of iron oxide with the active pigments in the experimental paints has greatly improved their performance on exterior exposure in Durban. This confirms observations made in a lecture to the Natal Branch of OCCA⁶⁵.

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Reviews

Rodd's chemistry of carbon compounds Volume IV—Heterocyclic compounds—Part B

Edited by S. Coffey,

Amsterdam, Oxford, New York: Elsevier Scientific Publishing Company 1977

2nd Edition. Pp 462. Price £41.00.

Rodd's Chemistry of Carbon Compounds has, of course, been a standard reference work for 20 years. It is, therefore, not surprising that a new edition has been produced of which this part is the most recent publication.

The pattern of the first edition has been followed, with Volume IV dealing only with heterocyclic compounds. It is interesting to note that the first edition managed to cover the subject in three parts, whereas the second edition will contain seven parts of which the first two cover 1112 pages, approximately one half the number in the whole of the first edition of Volume IV.

Rodd's work is, of course, a major treatise on organic chemistry and was the successor to Richter's Organic Chemistry which managed, in 1947, to cover the subject of heterocyclic compounds in less than 400 pages.

From the point of view of members of the Oil & Colour Chemists' Association, clearly, the volumes must have limited appeal and, bearing in mind also the cost, are unlikely to find their way into the libraries of any but the largest companies. As a reference work the series is, of course, invaluable.

The book under review covers the five-membered mono-heterocyclic compounds. For the first 235 pages alkaloids are covered which the reviewer found fascinating, especially the paragraphs on the Calabash-curare alkaloids.

For those interested in naturally occurring pigments, the chapters on the pyrrole pigments will be of value.

The book becomes of relevance to this industry with an account on phthalocyanines. Here, the writer refers to the first observation being made during the manufacture of phthalimide from phthalic anhydride and ammonia at the works of Scottish Dyes, Grangemouth, although recognition of the earlier work by other workers is noted. Although the writer comments on the process for manufacture using phthalic anhydride, urea and cupric chloride as a catalyst, phthalocyanines are also manufactured using phthalonitrile and copper salts. An interesting piece of information is the reference to the use of copper 4-monochloro-phthalocyanine to prevent the growth of the beta form in contact with the solvents. It is stated in the volume that halogenation can proceed to the introduction of between 15 and 16 atoms of halogen. This is theoretically possible but in practice the maximum is probably 14 and the yellower shades contain only 11 atoms of halogen (9 bromine, 2 chlorine).

This indigo is discussed only as a dye, although Pigment Red 198 (73390) was discovered by Schmidt, Bryk and Hoffa in 1906. Admittedly it was not until after the second world war that materials became commercially available.

The volume could be of more interest to the dyestuffs industry as there is a considerable amount of information on indigo and cyanine dyes but, regrettably, the amount of information on pigments is very limited and it is unlikely that members of OCCA will be compelled to refer back to such a fundamental work when there are available volumes dealing with the subjects of interest to the industry in much greater detail.

It would be expected that Rodd's Chemistry of Carbon Compounds will be on the bookshelves of all major reference libraries likely to be used by chemists.

G. E. WESTWOOD

Polymers for carbon papers and the reprographic industries

By H. Warson

Solihull Chemical Services, 1976.

Pp ix + 187, Price £50.00 (ISBN 0 905827 00 7)

Books about carbon papers and the reprographic industries are fairly rare, particularly the former.

The title of this book might lead one to hope that it would be a description of recent techniques in the industries involving application of polymers to them. It is, in fact, primarily a thorough search report of the literature, mainly as patents, as it exists in a number of modern industrial countries. As such, it has been very well done within the areas set out. The reader is presumably required to look up the reference concerned, after reading the brief summary, in order to determine how, or if, the information can be used.

It is intended to fulfil the need for a comprehensive study of the application of polymers to copying media and to be useful to chemists in the polymer and reprographic organisations as well as technical universities and polytechnics. No attempt is made to distinguish between those patents which have been developed into successful products and those that have, for one reason or the other, fallen by the wayside. To do so would have been very difficult, but the absence of any such guidance considerably reduces the value of the book.

There are some surprising omissions, such as polymers in modern typewriter ribbons and the pressure generation of electrostatic masters and copies, of which the former is well exploited commercially.

The book was not easily readable as, although divided into chapters and sections, each chapter being introduced by a page or so of description of the general technique used, it was seldom possible to follow any flowing sequence. As a report it is both useful and worthwhile.

There are several mistakes, most of which were printer's errors and the quality of printing is not good. References, which follow each chapter, identify the patents, journals or books mentioned in the text but there is no index. This, which could take various forms, is in the reviewer's opinion, a serious omission.

J. A. SEAWARD

Natal

Polyester wood finishes

A meeting of the Natal Section was held on Tuesday 22 February at the Ocean Terminal Restaurant, Durban, when 33 members and guests were present to hear a lecture on "Polyester wood finishes" presented by Mr P. A. Johnston.

Mr Johnston amplified the title by stating that he would deal with factors affecting curing rates of unsaturated polyesters and their influence on polyester wood finishes. An unsaturated polyester resin is a solution of an unsaturated polyester in an unsaturated monomer. The polyester itself is a compound composed of three basic materials, viz. a polyol, a saturated poly-carboxylic acid and an unsaturated poly-carboxylic acid. By varying the types of raw materials and the proportions in which they are used, an influence can be exerted upon their rate of reaction. Three important ancillaries that are used with polyesters are inhibitors, accelerators, and catalysts. Graphs and tables of results were presented which showed how gel times and cure rates may be adjusted by varying catalyst concentrations and by varying inhibitor/accelerator systems. An example was shown of how a resin with a gel time of 8 mins and a time to complete ambient cure of 480 mins can so be maintained that the gel time (or usable life) is extended to 34 mins, whilst the time to complete cure is reduced to 300 mins. Results were also quoted to illustrate the effect of heat upon gel times and cure rates. It is found that for every 5°C increase in temperature, the gel time is reduced by approximately 30 per cent whilst the cure time is reduced by approximately 20 per cent.

Polyester wood finishes form an important part of the furniture finishing market due to advantageous parameters of high build (500 micron), rapid cure, mar resistance, water and solvent resistance and high gloss. The main reason for their limited use is the volatility of suitable monomers. This volatility leads to problems of pollution of atmosphere, fire hazard and insufficient monomer remaining in film to effect complete cure.

These wood finishes are applied by both spray and curtain coating means. Single pot guns, single pot guns with both internal and external catalyst injection and twin pot systems are used, as are both single-headed and double-headed curtain coaters. Films are applied as either a single layer of an accelerated and catalysed resin or in the form of a layer of an accelerated resin followed by a layer of catalysed resin. In the latter instance, it is found that sufficient radical migration occurs providing the individual layers do not exceed 10 mil in cross-section. More recent curing methods developed are those methods that utilise high energy radiation to promote cure. The first of these methods, electron beam curing, relies solely upon the high energy radiation to break chemical bonds and so initiate the copolymerisation reaction. The equipment required for the production of this radiation is very expensive and this process is not used in South Africa.

The second radiation-induced process is that of ultra-violet cure. In this instance, a photoinitiator is incorporated in the resin. This photoinitiator absorbs ultraviolet radiation and dissociates to create free radicals in the system. This process is commonly used in South Africa, offering as it does the possibility of very rapid cure and reasonably low cost.

Industrial Finishes

A meeting of the Natal Section was held on Wednesday 9 March at the Ocean Terminal Restaurant, Durban. 37 members and guests were present to hear a lecture entitled "Industrial finishes with high solids polyurethane systems" by Mr Wieczorrek.

Low-solvent and solvent-free materials for the most varied of uses have been known for many years, and recently the attempts to extend the high-solids principle to light-stable and weather-resistant DD coating formulations with a solid content of 80 per cent and more were successful. The conventional structural principle of the D/D coating systems is basically retained; only their solvent content is reduced. The report dealt with the economics of the new system, their advantages and disadvantages and their application technology.

Firstly, difference between high-solids DD coatings and conventional coating systems: (i) At application viscosity the solids content of the new coating systems is between approx. 70 and 90 per cent by weight; (ii) The curing process is based on a polyaddition reaction, therefore, the high solids content of the coatings corresponds to their stoving residue; (iii) On account of their low content of volatile components, high-solids coating systems show little physical drying; (iv) Forced drying is indispensable, but through-hardening is independent of the oven residence time; (v) High-solids coating systems show comparably little shrinkage.

Secondly, economy: (i) Because of the high solids content it is possible to reduce the passes of spray application, and it may also be possible to reduce the number of coats; (ii) Solvents are expensive yet useless components of coatings; (iii) The physical and chemical properties are reached automatically during the first two weeks. Terms such as "underbake" or "overbake" are unknown here. Stoving is only to attain adequate surface hardness; (iv) The use of high-solids DD coatings permits the energy costs to be substantially reduced; (v) There is no condensate formation in the oven, therefore, the air requirements can be reduced; (vi) Reduced problems of waste disposal.

Mr Wieczorrek summed up the disadvantages as: (i) The raw materials prices for DD coatings are about 30 per cent higher than for conventional stoving finishes; (ii) Two-pack systems are involved; (iii) New investments for the two-part spraying unit.

and the advantages as: The quality of high-solids coatings correspond with the conventional coating systems; (i) Good build, excellent flow and resistance and light stability; (ii) high-solids coating systems back up the worldwide efforts of environmental protection by containing little solvent.

Mr Wieczorrek emphasised the importance of application at a stage of sufficiently low viscosity so that spray equipment can be used, but the two components must be thoroughly mixed together. He described a two-part spray unit using mixing tubes which is ideal and poses no problems in colour change.

The presentation ended with a very forceful slide show with taped commentary.



Arrangements for OCCA-30

The Exhibition Committee announces that the thirtieth annual exhibition of raw materials, plant and equipment for the paint, printing ink, colour and allied industries organised by the Association will be held at Alexandra Palace, London N22 from 18-21 April 1978.

Whilst the Committee naturally encourages the showing of new products, it does not stipulate that a new product has to be shown each year, since it fully appreciates that there are occasions when this is not possible. Accordingly, the Committee draws attention to the fact that new technical data on existing products are regarded as acceptable subject matter.

Motif for the Exhibition

The motif, designed by Robert Hamblin, uses the symbol of a moving indicator on a calendar to emphasise the importance of the continuous dialogue year by year between suppliers and manufacturers. The inward pointing letters recall the international aspect of this unique annual focal point for the surface coatings industries which in 1977 attracted visitors from 50 countries. The colours of the motif shown on the advertisement on the back outside cover of this issue will be carried throughout the publicity leading up to the Exhibition. The two main colours of the motif, royal blue and yellow, will be incorporated on the facias of the stands and it is intended to organise complementary flower displays in the Exhibition Hall. The use of these colours will create a pleasing contrast as visitors move from corridor to corridor at the Exhibition, as the royal blue colour will be used from east to west and the yellow colour from north to south.

Invitation to Exhibit

Copies of the Invitation to Exhibit have been despatched to companies and organisations in the UK and overseas which have shown at previous OCCA Exhibitions or

The cost effective Exhibition

have requested information for the first time for the 1978 Exhibition. Completed application forms for stand space must be returned to the Director and Secretary of the Association **not later than 1 October 1977**. The interest shown in the OCCA-30 Exhibition as a direct result of the highly successful OCCA-29 Exhibition held in March this year has been considerable, and already companies have asked for larger

OCCA-30 Exhibition

Alexandra Palace, London. 18-21 April 1978

The continuous dialogue

in the

surface coating industries

stands than they have had in previous years.

The Exhibition Committee was particularly pleased to see the large number of overseas companies showing at OCCA-29, both directly and through their British associates, and this emphasises the international character of the function.

The crowd puller

Visitors at OCCA-29 are known to have come from at least 50 countries and admissions of over 10,000 were recorded at the entrance. Any organisation wishing to exhibit at OCCA-30 should write immediately for details to the Director and secretary of the Association to receive a copy of the Invitation to Exhibit.

Facilities at Alexandra Palace

The Association has full use of the facilities at Alexandra Palace during the period of the Exhibition which include restaurants, two bars, a cafeteria and an exhibitors' bar. Another facility which is of considerable benefit to those travelling to the Exhibition by car is the ample free car parking space within the Palace grounds and the major routes to Alexandra Palace can be seen on the map opposite.

For visitors travelling to the Exhibition on the underground system, the Association will once again be running a free bus shuttle service to and from the Exhibition from Turnpike Lane Station on the London Underground Piccadilly Line. It is hoped that by the time of the Exhibition the extension of the Piccadilly Line to Heathrow Airport will be completed so that visitors flying into the country will be able to travel direct from the Airport.

Exhibitors were allowed for the first time in 1977 to serve alcoholic refreshments on their stands and this innovation will be continued at OCCA-30. Many exhibitors expressed their appreciation of this as it allowed their personnel to remain on the stands with visitors for the whole period of the Exhibition.

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.

Official Guide

This unique publication contains descriptions of all companies and their exhibits at the Exhibition and is issued to each Member of the Association at home and abroad together with season admission tickets. As in 1977, several Sections will be organising coach parties to visit the Exhibition and any Members interested should contact their local Section Hon. Secretary. (Full Section Committee lists for 1978 will be published in the August 1977 issue of the Journal.) It is also hoped that several parties will be organised from overseas to visit the Exhibition.

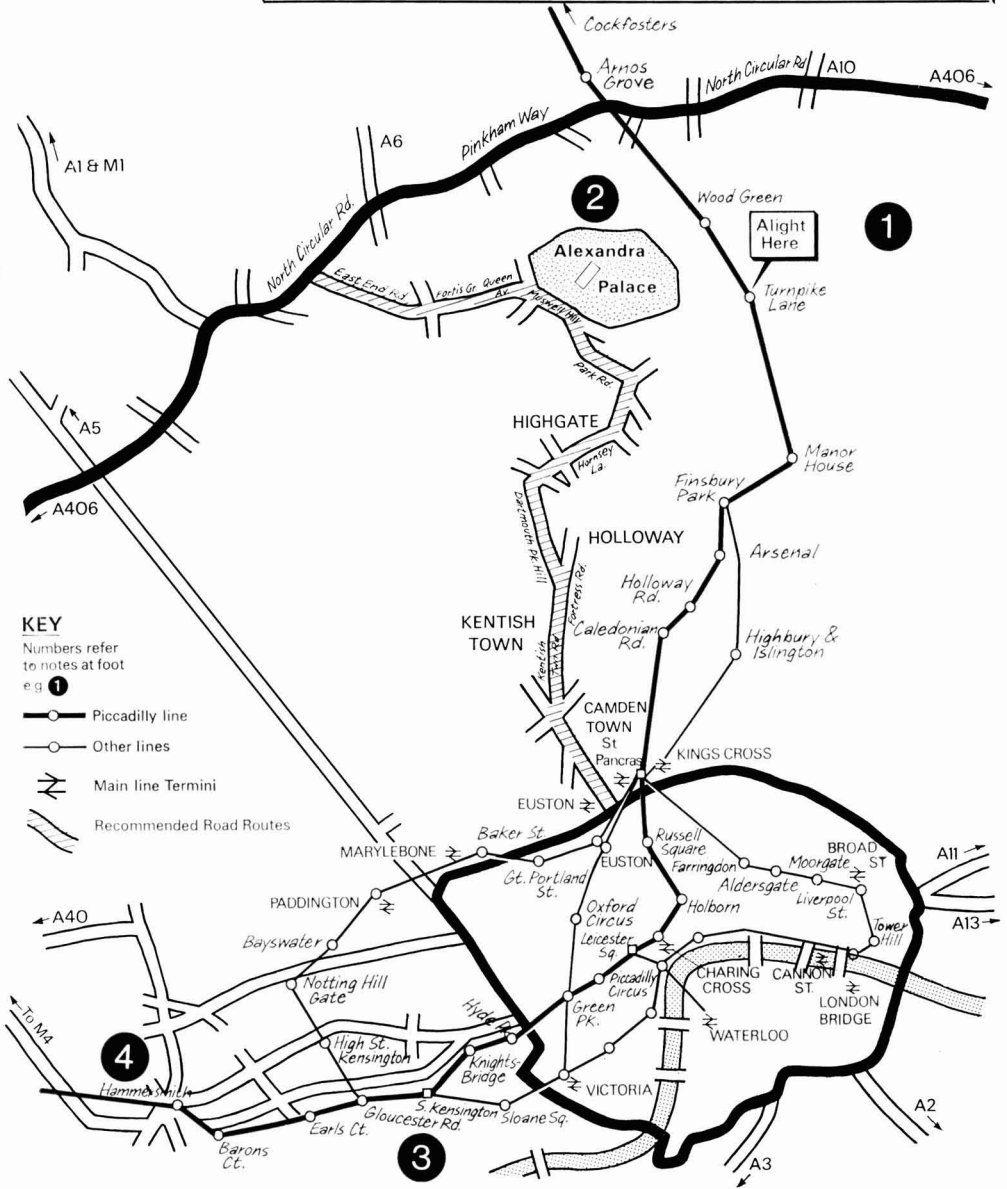


Visitors to OCCA-29 came from 50 countries

Advertising space is available in this important publication to both exhibitors and other organisations which are not able to show at the 1978 Exhibition. The Official Guide will be published early in 1978 so that visitors can obtain copies and plan the itinerary for their visits. Clearly, the Official Guide is a publication that will constantly be referred to both before and after the Exhibition and consequently any company wishing to advertise in the Guide should book space as soon as possible. Details of the advertising rates are available from Mr D. M. Sanders (Assistant Editor) at the address on the contents page. As in previous years the Official Guide and season admission tickets will be available several weeks in advance of the Exhibition (pre-payment only) from the Association's offices but they will also be available for purchase at the entrance to the Exhibition Hall. A charge is made for both the Official Guide and the season admission tickets to the Exhibition. The policy was introduced several years ago to deter casual visitors who otherwise collected large quantities of technical literature from exhibitors stands; the policy has been welcomed by exhibitors and has in no way acted as a deterrent to bona fide visitors to the Exhibition.

OCCA-30

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. See also the enlarged map of Alexandra Palace, reproduced on page 272.



KEY

Numbers refer to notes at foot e.g. 1

—●— Piccadilly line

—○— Other lines

⊕ Main line Termini

▬▬▬ Recommended Road Routes

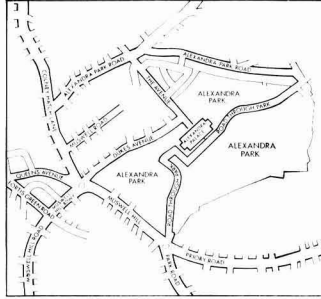
1. A free bus shuttle service will operate between Alexandra Palace and Turnpike Lane station on the Piccadilly Line (Underground), which is denoted by the thick coloured line. Destinations of trains may be marked as "Cockfosters" or "Arnos Grove" or "Wood Green",
2. Those travelling by road will find free car parking facilities at Alexandra Palace. See map on page 272.
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 Autumn 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 mainline stations in relation to the Piccadilly Line.

Continued from page 270

The international forum for the surface coatings industries

The Exhibition affords an ideal opportunity for an annual meeting of technical personnel at all levels in the supplying and manufacturing industries from all parts of the world to discuss their requirements and technical problems.

Alexandra Park and locality



There are adequate car parking facilities available at Alexandra Palace. Visitors travelling by road may consult the simplified diagram on page 271 showing the approach roads from central London and the motorways, and the enlargement above, of the area around Alexandra Park. The entrance through Dukes Avenue is for pedestrians only.

News of members

The following members of the Association have received new appointments in a recent reconstruction of the Burrell Colours Ltd UK sales force.

Mr S. Dray, an Ordinary Member attached to the Thames Valley Section, has been appointed as Area Manager for printing inks.

Mr S. Manning, an Associate Member attached to the Manchester Section, will serve major paint manufacturers through-

out the UK and Mr A. Smith, an Ordinary Member attached to the Midlands Section, has the task of extending Burrell Colours influence with the plastics industry.

Mr D. Gregory, an Ordinary Member attached to the Manchester Section, is the company's representative in the North of the country and Mr M. Barker, an Ordinary member attached to the London Section, is the technical representative for the Southern office.

Cape Section

Activities of the Eastern Cape Branch

Information has been received that three lecture meetings have now been held in Port Elizabeth where it is proposed to form an Eastern Cape Branch of the Cape Section.

The three meetings, which were all well attended, were addressed by Mr J. Gush of SA Tioxide Ltd on "Titanium dioxide in air drying gloss paints", by Mr D. J. Pienaar, a Vice-President of the Association, whose talk was entitled "Standardisation—quo vadis?" and by Mr Wiczorreck of Bayer AG on "Industrial finishes with high solids polyurethane coatings".

An acting Committee has been formed for the Branch consisting of the following members:

L. L. Hagemann Chairman
A. D. Price Hon. Secretary & Publications Officer
D. M. Lindsay Hon. Treasurer
R. Meyer
D. Bett
H. Potgieter

and all those interested in future branch activities should contact Mr A. D. Price at 54 Paterson Road, Port Elizabeth.

Upon the occasion of the Queen's Jubilee, the President and Council of the Association sent the Loyal Address shown *top right* to Her Majesty, and a reply was received from the Secretary of State for the Home Department, shown *bottom right*.



Forthcoming Events

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

Manchester Section

The annual competition for the OCCA Golf Trophy will be held at Stockport Golf Club, Offerton, Stockport on 7 September 1977. The competition is open to all OCCA Members, and there is a visitor's prize for guests. Further details may be obtained from Mr J. H. Sinclair, Anchor Chemical Co. Ltd, Clayton Lane, Clayton, Manchester M11 4SR.

Auckland Section

The fifteenth annual conference of the New Zealand Sections will be held at Rotorua on 28-31 July 1977 covering the technical and business aspects of the surface coatings industries.

Newcastle Section

Second UV Symposium—September 1977

A second symposium entitled "UV polymerisation and the surface coatings industry", sponsored by the Newcastle Section of the Association, is to be held at the University of Durham on 14 and 15 September 1977. Delegates staying at the University will assemble on the evening of 13 September and disperse on the evening of 15 September. Papers are to be presented by industry covering the practical aspects of the rapidly developing technique of UV curing. Topics will include photoinitiated polymerisation, UV curing equipment, photoinitiators and photosensitive monomers. Further details may be obtained from Mr H. Fuller, Tioxide International Ltd, Carlton Weathering Station, Yarm Back Lane, Stockton on Tees, Cleveland TS21 1AX.

Information Received

New laboratory

Neotec, who specialise in colour testing and matching instrumentation for quality control, have opened an international office and applications laboratory in the United Kingdom. From this office Neotec will operate directly in the UK and will work with their agents and representatives throughout Europe, Africa and the Middle East. The address of the office is 62 Norden Road, Maidenhead, Berkshire.

Sales expansion

Burrell Colours Ltd has restructured its UK sales force to improve the service to the paint, printing ink and plastics industries. Mr S. Dray has been appointed to the new position of Area Manager for printing inks, Mr S. Manning has been appointed to serve major paint manufacturers throughout the UK and Mr A. Smith has the task of extending Burrell Colours influence with the plastics industry.

New division

The adhesives manufacturers, Pafra Ltd, have announced the formation of a new division to develop and market quality and process controls, instruments and plant for use in the manufacture of all types of liquids in the adhesive, paint and chemical industries. The new division will be able to supply know-how to the industries, both in terms of software and hardware for the manufacture of products in liquid form to a high standard of regular consistency. The division is expected to be able to offer its services and new techniques to the industry by early in 1979.

Windows plant

British firms have designed and manufactured what is claimed to be the most advanced plant of its type in Europe for the automatic application of acrylic paint to aluminium extrusions. The plant, to be used by Crittall Windows Ltd, is expected to increase productivity and result in windows of a high quality finish. The process employed is known as electropainting and gives a consistent finish of a uniform thickness.

New colour lab

The Sun Chemical Corporation (Pigments Division) have opened a new technical service laboratory in Mitcham fully equipped to provide full spectrum service for the ink, paint and plastic industries. Among the services which the new facility will provide are colour analysis and matching, custom formulating and technical assistance for customers' problems.

AEI change name

AEI Scientific Apparatus Ltd, acquired in September 1976 by the US Instrument company Kratos, has changed its name to Kratos Ltd. Development and manufacture of the company's products range of scientific equipment will remain at the current premises in Manchester.

Arakawa changes name

Arakawa Forest Chemical Industries Ltd, a manufacturer of rosin derivatives and hydrocarbon resins, has changed its name to Arakawa Chemical Industries Ltd. The firm is remaining at the same address in Japan.

Design Council Award

Perkin-Elmer Ltd has won a second Design Council Award in five years for its high precision analytical instruments. This year the Award is being made for the Model 580 Ratio Recording Infrared Spectrophotometer.

Improved dispersions

Beken Engineering have developed a new Plantex intensive planetary mixer to improve dispersions, ensuring repeatability and increased capacity of master batch blending of all pigments. The new big mixer is presently being used by Plastic Coating Systems of Carnham and is the key to their present expansion programme.

Pressure sensors for ICI

The Reiss Engineering Co. Ltd have supplied over 100 Full-Stream pressure sensors for the new dyestuffs intermediates plant under construction by ICI in Scotland. The pressure sensors are used to combat the impedance to flow in liquid lines and to monitor the pressure of corrosive liquids and slurries.

High quality filters

Glen Creston Instruments Ltd have been appointed exclusive distributors in the UK and Switzerland for Grubb Parsons optical filters, mirrors, beam splitters, laser mirrors and coating service.

Double-figure growth

Drynamels, the Tube Investments powder coating company, are expected to grow by between 25 per cent and 28 per cent in volume this year compared with last year due to recent expansions at the company's plant.

SRL expand

Synthetic Resins Ltd have constructed new warehousing and distribution facilities at their Liverpool factory. The facility is designed to handle increasing business activity and to provide customers of an extended product range with an efficient delivery service.

Burrell expansion

Burrell Colours Ltd are constructing a new manufacturing and effluent plant at their Stockport works and are installing equipment for the making, filtering, drying and blending of an enlarged tonnage of the company's Fastona pigment range. The plant is expected to go on stream early next year.

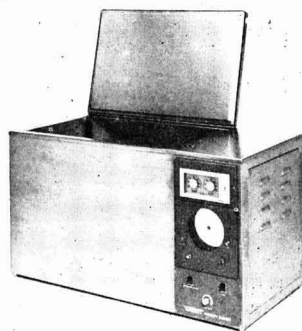
New products

New IR analyser

Wilks Scientific Ltd have introduced to the UK the Model 80 computing infrared analyser which enables the throughput of quantitative analysis to be dramatically increased. The Wilks Model 80 combines a high performance single beam infrared spectrometer with a programmable mini-computer, resulting in a completely new quantitative analysis system with unmatched speed and versatility. Solid, liquid or gaseous samples are accepted by the instrument without the need to vapourise or dissolve them or separate them into their individual components.

New humidity cabinet

John Godrich has available the new Credit humidity cabinet for humidity and



condensation tests which conforms to the requirements of BS 3900 F2. The standard model is fitted with a temperature cam operating time/temperature programmer capable of functioning within the range of 30°C-80°C.

New pigment dispersions

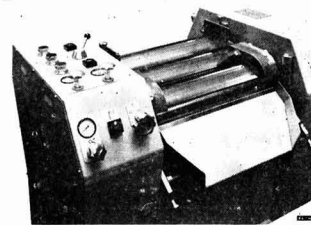
The Inmont Corporation have available a new series of multi-purpose pigment dispersions, marketed under the name "RBH 221", in a range of 12 colours. Specifically designed for use in a wide range of industrial coatings and for application on virtually all industrial substrates, the versatile new dispersions offer compatibility with many different vehicles.

Textured finish

BASF have available Acronal 567 D ca. 50%, a finely dispersed acrylic copolymer dispersion with medium viscosity and a low film-forming temperature. It is primarily intended for the production of textured finishes, indoor paints and primers for various substrates, and has high flexibility and resistance to water.

Triple-roll mill

Buhler-Miag Ltd have available their improved design of the well-known hy-



draulic three roll mill SDX-600, which has an output increase of 30 per cent for inks and paints etc.

Colour matching cabinet

Ultra-Violet Products Ltd have available a new UVP colour matching cabinet which is a fast, simple colour matching system specifically designed to aid in the visual identification of potential colour mismatches. It is ideally suited for mixing and matching paints, dyes, inks, textiles, plastics and coatings especially where it is

required to match a customer's sample when the pigments or formulation are not known. Unique lighting system detect metamorphism and eliminate time consuming matching under a multiplicity of lamps. Other features include instant-start operation and a tilting sample holder to alter the viewing angle and reduce reflection.

Hydrocarbon resins

A new range of hydrocarbon resins produced by Faime S.p.a. of Italy and marketed under the tradename "Resen" are being exclusively introduced to the UK by Albright & Wilson. The resins are of 100 per cent hydrocarbon composition and are essentially aromatic-olefin condensation products with excellent solubility and compatibility characteristics. They possess very low acidity and may be used with a wide range of pigments without danger of gelling, pigment damage or colour change.

Paint additives

The organic products division of Henkel & Cie GmbH have introduced two new paint additives, PV Perenol S4 and VP Perenol S5, to improve surface smoothness and to increase resistance against scratching and abrasion. The active ingredient is a solvent containing modified polysiloxane for which the approval of the Health authorities has been obtained.

Air-operated transfer pump

Loba Industrial Products Ltd have available a new smaller version of the Wilden air-operated glandless double-diaphragm pump known as Model M4. Its pumping capacity can be controlled by the adjustment of an air valve to give volumes from a few litres up to 270 litres per minute maximum. The pump is suitable for handling clear liquids or thick abrasive and corrosive slurries containing up to 90 per cent solids.

Carbon black pastes

Degussa have available new carbon black pastes designated UD 20/P 200 and UL 20/T for the colouration of polyurethane foams which are extensively used in the manufacture of armrests, upholstery, dashboard facings, steering wheel covers, headrests etc. in the motor industry.

New in-can preservative

Sterling Industrial have formulated a new in-can preservative, Parmetol A23, specially designed to prevent the occurrence of bacteria and fungal growth, thereby prolonging the shelf life of aqueous based products.

UV-Vis spectrophotometer

Perkin-Elmer have available a new dual wavelength double-beam UV-Vis spectrophotometer, the Model 556, ideally suited for application involving turbid samples, mixture analysis and many other biochemical and industrial applications.

Conferences, courses etc.

Durability of building materials

The National Research Council of Canada is organising an international Conference on the "Durability of building materials and components" to be held in August 1978 in Ottawa.

Chemical education

The International Union of Pure and Applied Chemistry is organising a Conference on "Chemical Education in the coming decades—problems and challenges", to be held in Ljubljana, Yugoslavia in August 1977.

Finishing conference

The Association for Finishing Processes of the Society of Manufacturing Engineers will hold "Finishing 77" with the theme 'Finishing in the new environment' in October 1977 in Detroit, Michigan.

Pigments school

The University of Leeds is organising its third Pigments School to be held in September 1977 at the University.

Literature

Hydrocarbon solvents

The Hydrocarbon Solvents Association Ltd have published a booklet which is a guide to the safe handling of the hydrocarbon solvents manufactured and marketed by its members.

Emulsion polymer products

Scott Bader have available a leaflet describing their emulsion polymer products and their recommended applications.

Precious metal preparations

The Ceramic Colours Division of Degussa have published in German and English a new information bulletin for customers concerning precious metal preparations for screen printing, which presents the main bright and burnishing preparations of the Degussa range giving instructions of their correct use.

Industrial chemicals

Jordan Dataquest have published their survey of industrial chemical firms providing profiles of the financial states of the companies involved.

Register of Members

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

Ordinary Members

- ARMSTRONG, COLIN, PhD, BSc, Coates Bros (SA) Ltd, 18th Avenue, Maitland, Cape 8000, South Africa. (*Cape*)
- BEATSON, IAN DAVID, MSc, 102 Ravenwood Drive, Forrest Hill, Auckland 10, New Zealand. (*Auckland*)
- BETT, DUGALD DOUGLAS, 21 Bunting Crescent, Cotswold Ext, Port Elizabeth 6001, South Africa. (*Cape*)
- BILEFIELD, LIONEL IVOR, BSc, MA, Paintmakers Association, Alembic House, 93 Albert Embankment, London SE1 7TY. (*London*)
- DAY, ROBERT EDWARD, PhD, BSc, 16 Thweng Way, Guisborough, Cleveland TS14 8BW. (*Newcastle*)
- EDGE, JOHN ROLAND, 50 Rue du General de Gaulle, 27100 Le Vaudreuil, France. (*General Overseas*)
- EMMERSON, STEWART FRANK, 75 Studdon Walk, Newcastle upon Tyne 3. (*Newcastle*)
- GRAVES, ROY EDWIN, Robert Bryce & Co. Ltd, 72 Hayr Road, Mt. Roskill, New Zealand. (*Auckland*)
- GUNN, DAVID JOHN, 147 Redhill Road, West Heath, Birmingham B31 3ND. (*Midlands*)
- HAGEMANN, LEONARD LUKE, BSc, Prolux Paints (EP) (Pty) Ltd, PO Box 2099, Port Elizabeth 6056, South Africa. (*Cape*)
- HAMILTON, ALEXANDER JOHN FOX, 18 Ridlands Rise, Limpsfield Chart, Surrey RH8 0TS. (*London*)
- HOWELL, DAVID MAURICE, Macpherson Powders Ltd, Jenkins Lane, Barking, Essex. (*London*)

- KEMP, ROY ARTHUR, BSc, Prolux Paints (EP) (Pty) Ltd, PO Box 2099, Port Elizabeth 6056, South Africa. (*Cape*)
- LEWIS, IAN DOUGLAS, BSc, 113 Matlock Crescent, Cheam, Surrey SM3 9SY. (*London*)
- NASH, JOHN ALFRED, PhD, BSc, 42 St. Augustines Park, Ramsgate, Kent. (*London*)
- POYNER, ALLAN HOWARD, LRIC, 19 Colenso Road, Blackburn, Lancs. (*Manchester*)
- ROURKE, JIM, 188 New Toronto Street, Toronto, Ontario M8V 2E8, Canada. (*Ontario*)
- TAPE, BRIAN WILLIAM CHARLES, 301 Allen Road, Hackettstown, New Jersey 07840, U.S.A. (*General Overseas*)
- WATSON, PETER WILLIAM, MSc, Metal Box Ltd, Kendal Avenue, Westfields Road, Acton, London W3 0RR. (*Thames Valley*)

Associate Members

- BROTHERS, ROY STEPHEN, 78 Marble Arch Cr, Scarborough MIR 1W9, Ontario, Canada. (*Ontario*)
- CURTIS, ROBERT, 101 Janefield Avenue, Guelph, Ontario, Canada. (*Ontario*)
- VALENTINE, WILLIAM PETER NORMAN, Vaughan Mason & Co. Ltd, 43 Stamford New Road, Altrincham, Cheshire. (*Manchester*)

Registered Students

- COOK, STEPHEN, 514 Bolton Road, Darwen, Lancs. (*Manchester*)
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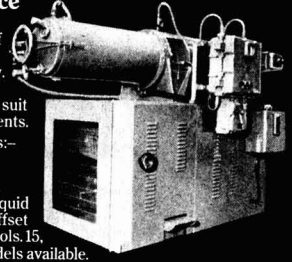
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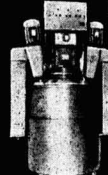
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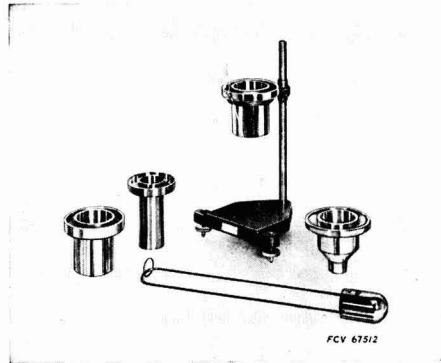
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