



OCCA-32 EXHIBITION

13-15 MAY 1980

NEW VENUE

Preliminary announcement page 270



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JOURNAL OF THE IL & OLOUR HEMISTS' SSOCIATION

Paint extenders based upon naturally occurring aluminium silicates (china clays)
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Electron-beam curing of coatings
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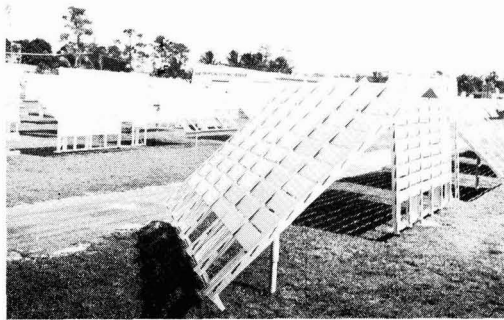
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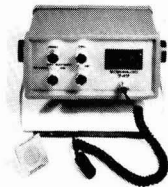
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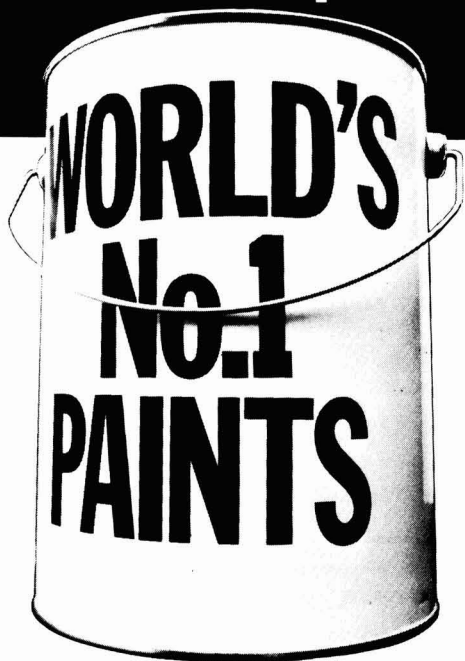
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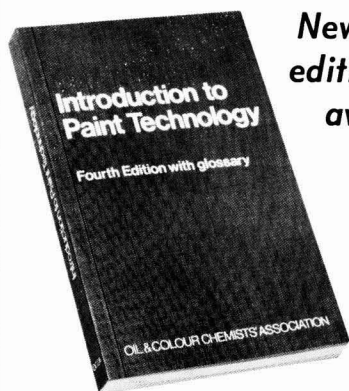
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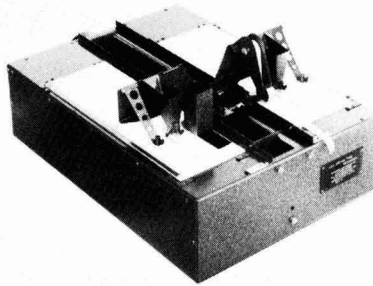
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Paint extenders based upon naturally occurring aluminium silicates (china clays)*

By **D. J. Huxtable and F. G. Pickering**

ECC International Ltd, St. Austell, Cornwall

Summary

China clay is defined and an outline of the principle aqueous extraction system used for its preparation in the United Kingdom is given. Information regarding the nature and size of china clay particles is linked to its performance properties in paint.

The effects of heating china clay to temperatures of up to

1100°C are described, and the resultant properties of commercial products (china clays) are discussed.

Some current development work is reviewed with emphasis on the particle size effect of flash calcined clay in paint.

Keywords

Types and classes of coatings and allied products

emulsion paint

Raw materials for coatings

extender pigments

extender pigment
china clay
aluminium silicate
calcined clay
kaolinite

Properties, characteristics and conditions primarily associated with

materials in general

viscosity
rheology

raw materials for coatings and allied products

particle size
hiding power

Matières de charge pour peintures à base des silicates d'aluminium d'origine naturelle (terres de porcelaine).

Résumé

On donne une définition pour la terre de porcelaine et on trace les grandes lignes du système d'extraction par voie aqueuse utilisée au Royaume Uni. Les données sur la nature et la granulométrie de la terre de porcelaine sont mises en rapport avec son comportement en peintures.

On décrit les changements provoqués en terre de porcelaine par calcination à des températures jusqu'à 1100°C, et l'on discute

les caractéristiques des produits de commerce (les terres de porcelaine) qui en résultent.

On passe en revue quelques études de développement actuelles et on souligne à l'égard des peintures, l'effet qu'exerce la granulométrie du kaolin "flash calciné", c'est-à-dire qui a été calciné aussi rapidement que possible.

Streckmittel für Anstrichfarben aus in der Natur vorkommenden Aluminiumsilikaten (Kaolinen)

Zusammenfassung

Kaolin wird definiert, und das Prinzip des im UK benutzten Extraktionssystems mittels Wasser kurz beschrieben. Information über die Art und Grösse von Kaolinpartikeln wird in Beziehung gebracht mit ihrer Funktion in Anstrichmitteln.

Die Auswirkungen der Erhitzung von Kaolin auf Temperaturen bis zu 1100°C werden geschildert, und die sich daraus

ergebenden Eigenschaften für handelsübliche Kaoline werden besprochen.

Betrachtet werden auch neuere Entwicklungsarbeiten mit der Betonung der Auswirkung auf die Teilchengrösse von flashkalziniertem Kaolin in Anstrichmitteln.

China clay, a naturally occurring, hydrated aluminium silicate, is found in many parts of the world, but the most well known deposits are located in the USA and the south west peninsula of England. It is found in decomposed granite as the mineral kaolinite, together with quartz, mica and small amounts of other minerals. In the English

deposits the proportion of kaolinite in the granite matrix is approximately 15 per cent. Clay in this situation, that is when found in the place where it was formed, is known as primary clay. In some deposits the clay has been naturally removed from its original location and re-deposited in a form known as secondary clay. Products used in the paint

*Paper presented at the South African Division Symposium held at Cape Town on 2-5 November 1978.

industry are chiefly obtained from primary deposits.

Extraction

Although the following description has many general applications it is based specifically on the methods used in England (Figure 1).

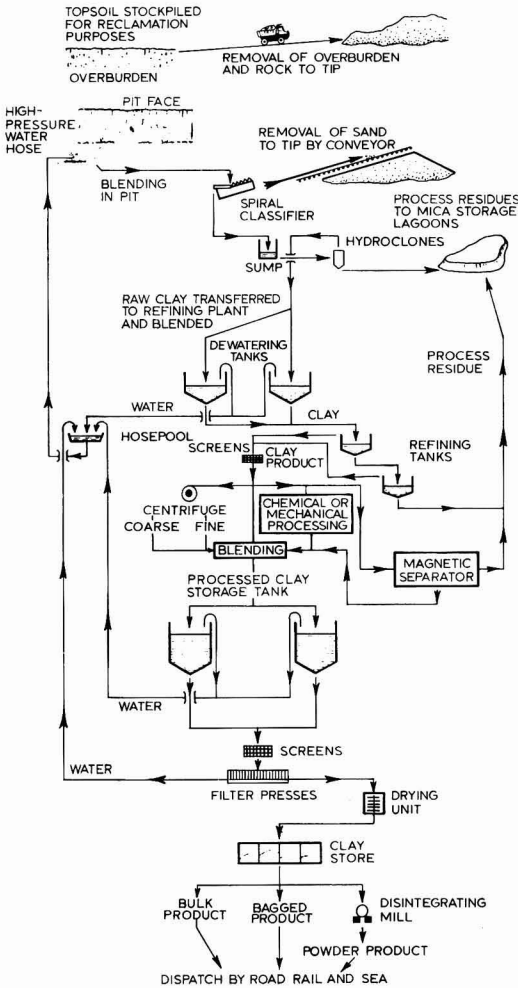


Figure 1. Production of English china clay

Commercial clay deposits are close to the earth's surface and are worked from open pits. After removal of overburden, the clay is washed from the kaolinised granite face by high pressure water jets. The clay slurry flows to the lowest point of the pit where a primary separation of coarse particles is effected by spiral classifiers. The coarse material (quartz) is removed from the pit by conveyor and the clay suspension is pumped to thickening or dewatering tanks. At this stage chemical deflocculants are added so that separation of specific particle size fractions may be achieved. This separation is brought about both by natural

sedimentation and high speed centrifuging. Ultimately a range of grades is produced, still in aqueous suspension, having closely controlled particle size distributions. These grades will vary with respect to surface area from 5 to 14 m²/gm.

The above techniques are now supplemented by many advanced methods of mineral processing (e.g. magnetic separation and froth flotation) and particle size may be further controlled by physical comminution.

Refining is followed by drying, a process which may vary in detail, but will normally involve a pressing operation, where moisture is reduced to about 30 per cent and a heating/pulverising process where moisture is progressively reduced to less than 1 per cent.

Subsequent handling takes many forms varying from the traditional 25 kg paper bag to bulk rail or road tankers.

China clay properties

A well formed china clay particle is hexagonal and plate-like in shape. The aspect ratio will increase as particle diameter is reduced, to a typical level of 10:1 and a maximum of about 20:1. Large particles normally exist in the form of stacks which can be likened to a pack of playing cards.

Many naturally occurring particles have a surface charge and usually this charge is negative, as in the case of most clays. Although the net charge is negative, a clay particle will have negative surface charge and positive edge charge. Thus, if suspended in water in this form, particles will exert edge to face attraction and structure will develop. In this form a clay suspension is flocculated. A deflocculated suspension is achieved by increasing the pH to a value greater than 7 and shielding the positive edge charges by absorbed polyanions (e.g. polyphosphates or polyacrylates) (Figure 2).

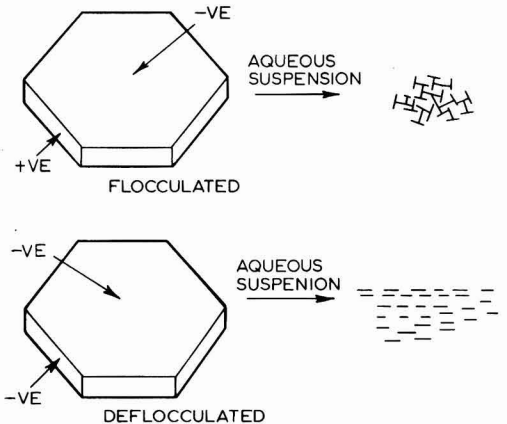


Figure 2. Idealised clay particles

As previously noted, the refining processes produce grades differing in particle size distribution. Other properties which will change with particle size are listed below:

Particle size becoming finer

- oil absorption is increased
- powder whiteness is increased
- water soluble salts are increased

Properties which are independent of particle size and normally constant are:

- density
- pH of the aqueous suspension
- moisture content

The pH of an aqueous suspension of clay in its natural form will be about 5 (floculated). Some clays are produced in what is often called predispersed form with aqueous pH values of 7–8 (Table 1).

Table 1
China clay properties

| | Fine clay | Intermediate clay | Coarse clay |
|--------------------------------|------------------|-------------------|------------------|
| Dry powder brightness | 89 | 86 | 80 |
| Specific gravity | 2.6 | 2.6 | 2.6 |
| Oil absorption g/100 g | 42 | 38 | 33 |
| pH of 10% aqueous slurry | 5.0 or 7.5 | 5.0 | 5.0 or 7.5 |
| % Moisture content | 1.0 max. | 1.0 max. | 1.0 max. |
| % Water soluble salts | 0.12 | 0.11 | 0.07 |
| <i>Particle size data</i> | | | |
| % Greater than 53 μ m | 0.01 | 0.02 | 0.03 |
| % Greater than 10 μ m | 0.2 | 12 | 19 |
| % Less than 2 μ m | 80 | 45 | 25 |
| % Less than 1 μ m | 60 | – | – |
| Surface area m ² /g | 11–12 | 7 | 5 |

Table 2
China clay performance
70% PVC emulsion paint pigment: Extender
volume ratio 1:6

| | Fine clay | Intermediate clay | Coarse clay |
|---|-----------|-------------------|-------------|
| Viscosity (poise) | | | |
| ICI Rot thinner – | | | |
| – Initial | 1.6 | 1.45 | 1.32 |
| – After 28 days | 1.5 | 1.2 | 0.9 |
| Paint film brightness | 89.8 | 87.2 | 84.1 |
| Contrast ratio (16 m ² /litre) | 94.8 | 91.5 | 88.1 |
| Specific gravity | 1.39 | 1.39 | 1.39 |

Properties in paint

It is possible to relate clay properties to performance in paint using the principle parameter of particle size. These relationships are general and not specific (Table 2).

Dispersion

China clays are hydrophylic and disperse readily in aqueous media. Fine clays disperse more readily than others. In alkyd paints, dispersion characteristics are linked more with dry aggregate size and strength, rather than with ultimate particle size.

Rheology

Increased viscosity and thixotropy are associated with decreasing particle size in all types of paint.

Gloss

Gloss is reduced as particle size is increased, despite the attendant reduction in binder absorption. Coarse particles produce a more uneven film surface which has the effect of randomising scattering the incident light and reducing specular reflectance.

Brightness

The contribution of an extender towards film brightness (and consequent whiteness) is linked to the dry powder brightness of the extender and, in the case of china clay, brightness increases as particle size is reduced. At lower PVC's the light scattering effect of fine particles contribute additionally to brightness.

Opacity

Finer particle size is associated with increased opacity. In some cases, however, coarser china clays may contain larger levels of light absorbing impurities than finer clays and this would contribute towards opacity. This would, however, have an equally adverse effect on brightness. Very fine particle size china clays contain a large number of particles with a face to face thickness which helps to promote optimum pigment particle spacing.

Weathering resistance

This property is adversely affected by reducing particle size. This is undoubtedly due to the higher oil absorption of these materials leaving less free binder for film forming properties.

Scrub resistance

As with weathering resistance and for the same reason this property is impaired as particle size is reduced.

Calcined clay

Ref. 1

When china clay is progressively heated, or calcined, it passes through four stages:

- (a) The removal of absorbed moisture which is complete at 150°C.

- (b) Dehydroxylation, an endothermic structural change, in which metakaolinite is formed and water evolved. The change will start at 500°C and is completed by 700–800°C.
- (c) A complete structural change between 800°C and 1100°C.
- (d) Above 1100°C mullite and silica are formed; the latter can be either amorphous or crystalline.

Calcined clays used in paint are all from group (c) above, in which the metakaolinite transformation is complete, but mullite formation has not commenced.

The variables in the calcination process are feedstock, time and temperature. In the case of English calcined clays, the feedstocks are fine particle size china clays, the temperatures are in the above noted range, but the residence time can vary from less than one second to more than one hour.

Calcined clays produced by a very rapid heating process (flash calcination) have opacifying properties in paint systems, together with decreased specific gravity. An explanation offered is that the outside of the clay particle becomes dehydroxylated before the inside. Thus water vapour is evolved inside a sealed particle giving an expanded structure with reduced specific gravity. Applications for this type of product are normally in alkyd paints.

A second process exposes clay to high temperature for longer periods and is known as soak calcination. In this product, clay particles appear to exist as aggregates or groups of fused individual particles with an open structure. Ultimate particle size is controlled by a dry milling process which preserves the open structure. This type of clay is most widely used in emulsion paints (Table 3).

Calcined clays—Paint properties

The performance characteristics of calcined clays in paint have been well described¹, and are easily demonstrated (Figures 3–6). Three clays were compared in a typical emulsion binder without using any prime pigment. Dry film brightness and opacifying properties were measured at PVC's ranging between 30 and 70 per cent. The above two types of calcined clay were compared with a fine particle size natural clay.

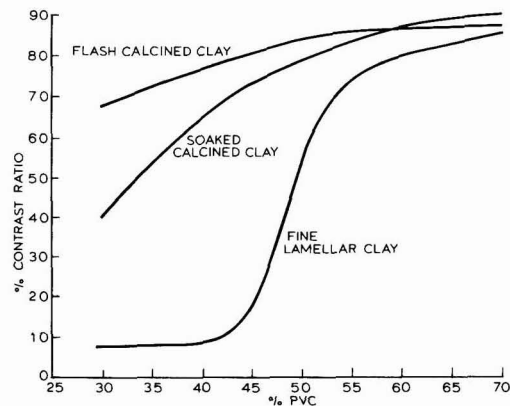


Figure 3. Hiding power in emulsion binder

Table 3
Comparison of properties of natural and calcined clay

| | Natural clay | Flash calcined clay | Soak calcined clay |
|---------------------------------|--------------|---------------------|--------------------|
| Dry powder brightness | 89 | 81 | 91.5 |
| Specific gravity | 2.6 | 2.1 | 2.5 |
| Oil absorption g/100 g | 42 | 69 | 49 |
| pH of 10% aqueous slurry | 5.0 | 5.0 | 6.0 |
| % Moisture content | 1.0 | 0.5 | 0.5 |
| % Water soluble salts | 0.12 | 0.17 | 0.32 |
| <i>Particle size data</i> | | | |
| % Greater than 53 μ m | 0.02 | 0.2 | 0.1 |
| % Greater than 20 μ m | 0.05 | 3.0 | 3.0 |
| % Greater than 10 μ m | 0.2 | 28 | 10 |
| % Less than 2 μ m | 80 | 25 | 50 (min.) |
| % Less than 1 μ m | 60 | 12 | 30 |
| Surface Area m ² /gm | 11–12 | 9.5 | 8.5 |

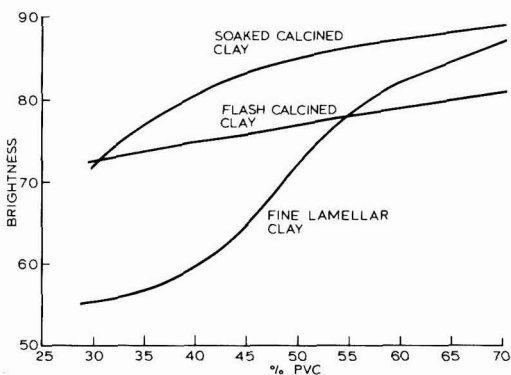


Figure 4. Film brightness in emulsion binder

Dry hiding was obtained from both calcined clays at low PVC's but from the natural clay only above the CPVC. The calcined clays contribution to opacity is due to entrapped air both in and between the clay particles. Film brightness measurements follow a similar trend and at high extender levels are clearly related to powder brightness values.

A similar comparison was made using an alkyd binder. In this case, only the flash calcined clay achieved a degree of opacity at low PVC. It is assumed in this case that the open structure of fused particles in the soak calcined clay is penetrated by the binder. In the case of flash calcined clay, the voids formed during calcination are impenetrable. With regard to film brightness, only the flash calcined clay is effective at low PVC's, but above the CPVC film brightness is ranked in the order of powder brightness.

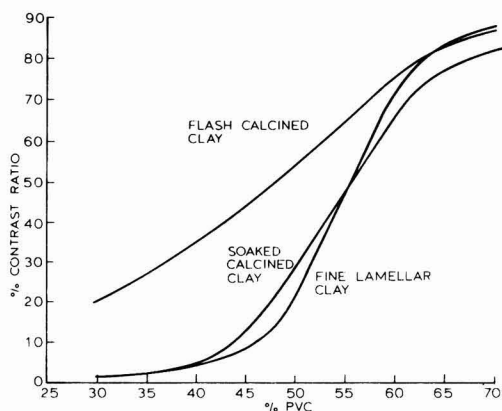


Figure 5. Hiding power in alkyd binder

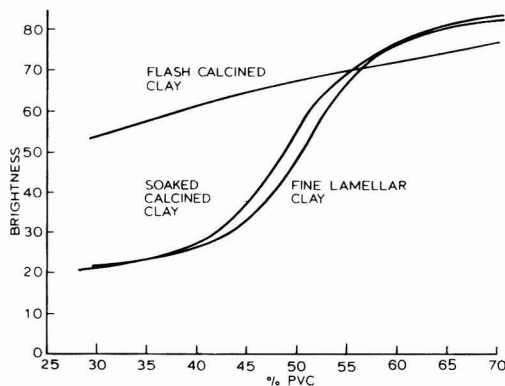


Figure 6. Film brightness in alkyd binder

Although optical properties are of prime importance, calcined clays are associated with other effects not all of which are advantageous. Higher film porosity can adversely affect stain removal and re-coatability. One significant advantage, however, is seen in durability, where because of the very hard nature of calcined clay particles the scrub resistance is very good.

It is obvious that calcined clays have technical advantages over natural clays (Table 4), but it is equally obvious that because of higher production costs they will be more expensive. Nevertheless, a comparison of extenders in paints formulated to give equivalent raw material costs demonstrates that calcined clays offer cost effective advantages (Table 5).

Developments

Ref. 2

These can be considered under three headings:

Raw materials

Reference was made earlier to new methods of mineral separation. These techniques may be used to improve

Table 4
Comparison of performance of natural and calcined clay

(A) 85% PVC emulsion paint. Pigment: extender volume ratio 1:10 (Extender 1:1, clay: whitening)

| | Natural clay | Flash calcined clay | Soak calcined clay |
|---|--------------|---------------------|--------------------|
| Viscosity (poise) ICI Rotthinner | 1.4 | 2.5 | 1.5 |
| Paint film brightness | 89.2 | 86.8 | 90.9 |
| Contrast ratio (16 m ² /litre) | 95.5 | 96.3 | 94.9 |
| Stain resistance | 36.8 | 32.7 | 26.1 |
| Scrub resistance | 4500 | 10,000 | 10,000 |

(B) Flash calcined clay in alkyd paint (50% PVC)

| Pigment: extender volume ratio | 1:1.8 | 1:2.3 | 1:3.2 | 1:4 |
|---|-------|-------|-------|------|
| Viscosity (poise) Rotthinner | 5 | 5 | 5 | 5 |
| Paint film brightness | 85.5 | 84.7 | 83.9 | 83.1 |
| Contrast ratio (16 m ² /litre) | 93.5 | 93.0 | 92.3 | 91.4 |

Table 5
Clay comparisons at equivalent raw material cost
70% PVC emulsion paint

| | Fine clay | Intermediate clay | Soak calcined clay |
|---|-----------|-------------------|--------------------|
| Viscosity (poise) Rotthinner | 11.5 | 11.8 | 8.4 |
| Paint film brightness | 92.0 | 91.7 | 92.9 |
| Contrast ratio (16 m ² /litre) | 96.1 | 95.8 | 96.3 |
| Stain resistance | 49 | 46 | 36 |
| Scrub resistance | 1500 | 1500 | 2500 |
| Pigment: extender volume ratio | 1:5.9 | 1:4.8 | 1:12.1 |

product purity and colour. The latter effect is advantageous with both natural and calcined clay, and has led to development products (calcined) with powder brightness values of 96 which represents an improvement of about 5 per cent.

Processing

Work has been published recently on the effects of particle size of flash calcined clay on its application properties in paint². It was noted earlier that flash calcination causes particle expansion and density reduction. Particle size fractions were prepared by fractionation and density was found to decrease with decreasing particle size (Figure 7). The weight loss due to dehydroxylation obtained by heating the flash calcined clay to 1050°C was plotted as a

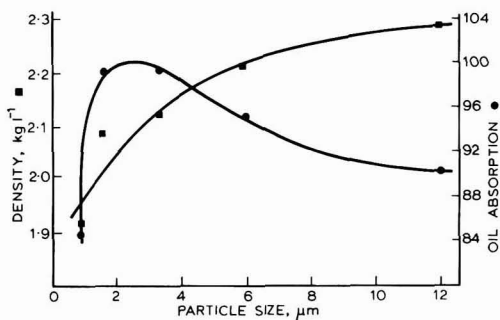


Figure 7. Variation of density and oil absorption with particle size

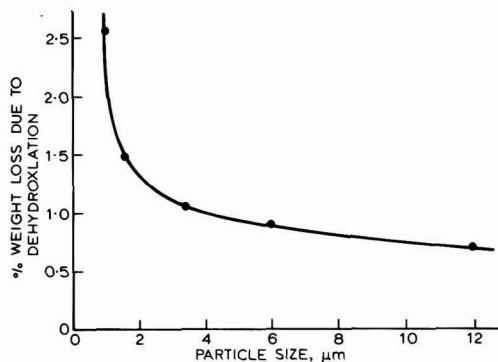


Figure 8. Variation of weight loss due to dehydroxylation with particle size

function of the same particle size fractions (Figure 8). It was clear that the degree of dehydroxylation achieved during the flash calcination process was greater with larger particles than with fine fractions. This was thought to be due to the fact that larger particles, having a higher thermal capacity, would take longer to reach the high temperature required for dehydroxylation than would small particles. Again it is probable that these large particles would remain at the higher temperatures for longer times than would small particles. This would lead to the presence of fewer voids in large particles, since very rapid heating is required to convert the outer layers of a china clay particle to a silicon aluminium spinel before the inner layers are dehydroxylated. It is calculated that at least 10 per cent of total water must remain in the kaolinite after surface dehydroxylation in order to create sufficient pressure to produce air voids. This would be represented by a weight loss of 1.2 per cent in Figure 8 corresponding to a particle size at $3\mu\text{m}$. It is probable, therefore, that particles larger than $3\mu\text{m}$ will contain relatively few voids. This argument, of course, will apply only to the particular process of calcination used in this work.

The optical properties of alkyd based paint films in which these fractions were incorporated (without prime pigment) are given in Figures 9 and 10, where it is seen that the finer fractions produce better film brightness and opacity.

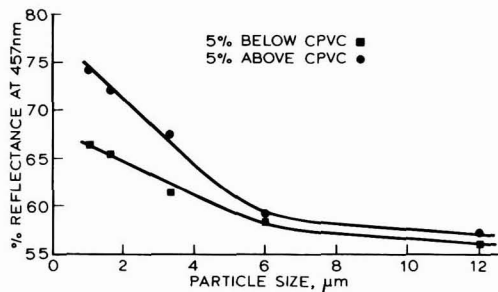


Figure 9. Variation of reflectance of paint film with particle size

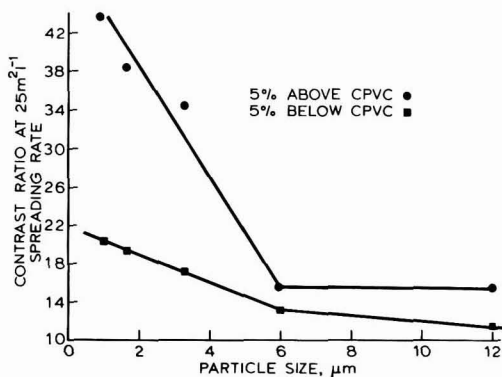


Figure 10. Variation of contrast ratio of paint film with particle size

Test Methods

Another current interest is in the development of a method for measuring opacity of extended paint film based on the Kubelka-Munk analysis of reflectance data. The opacity value measurements are expected to have a precision of 0 ± 0.5 units (95 per cent confidence level) and it is hoped that the results of this work will form the basis of a future publication.

[Received 6 February 1979]

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Electron-beam curing of coatings*

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Summary

The coating industry is constantly looking for more efficient and more rapid curing methods. One of these is the use of high-energy ionising radiation. Electron-beam accelerators are playing an ever-increasing role in the radiation curing of coatings on a variety of substrates, including some which are heat sensitive, e.g. timber and plastics, and where conventional stoving procedures cannot be applied. This new technique offers rapid curing at ambient temperatures and in many cases 100 per

cent solid systems for curing can be prepared, resulting in a decrease in solvent costs and ecological problems. In addition, electron accelerators take up very little space and production lines can be put into operation in a matter of seconds. Considering that this technique has relatively low energy requirements, all indications are that from an economic, ecological and performance point of view, electron-beam curing will play an important role in the future of coating curing.

Keywords

Processes and methods primarily associated with

drying or curing of coatings

electron curing
radiation curing

Miscellaneous terms

cost
investment cost
labour cost
operation cost

Le durcissement de revêtements par faisceaux d'électrons

Résumé

L'industrie de peintures cherche constamment les méthodes de durcissement à la fois plus efficaces et plus rapides. Parmi celles-ci on compte l'emploi de radiation ionisante à grande énergie. Les accélérateurs d'électrons jouent un rôle toujours en voie de devenir plus important dans le domaine du durcissement de revêtements appliqués à une gamme de supports, y compris certains qui sont sensible à la chaleur, par exemple, le bois et les matières plastiques, et où les procédés d'étuvage normaux ne sont pas admis. Cette nouvelle technique offre la possibilité d'effectuer le durcissement rapide aux températures ambiantes, et, en plusieurs cas, on peut préparer des systèmes qui ne contiennent pas de

matière volatile, qui sont aptes à être durcis par ce procédé, et qui assure une diminution du coût de solvants et également des problèmes écologiques. D'ailleurs, les accélérateurs d'électrons n'exigent pas beaucoup de place et on peut mettre en marche en quelques secondes les chaînes de production qui les incorporent. Compte tenu de la demande en énergie relativement faible de cette technique, il est probable en raison des avantages économiques, écologiques et du rendement, que le procédé de durcissement par faisceaux d'électrons jouera un rôle important à l'avenir dans le domaine du durcissement de revêtements.

Elektronen-Strahlenbündelhärtung von Lacken

Zusammenfassung

Die Anstrichmittel verarbeitende Industrie sieht sich ständig nach wirkungsvolleren und rascher arbeitenden Härtungsmethoden um. Dazu gehört der Einsatz von ionisierender Bestrahlung hoher Energie. In der Härtung von Lacken auf vielerlei Substraten, einschliesslich einigen hitzeempfindlichen, wie Holz und Kunststoffe, und solchen für welche konventionelle Ofentrocknungsmethoden nicht angewandt werden können, spielen Elektronenbündel-Beschleuniger eine immer bedeutender werdende Rolle. Diese neue Technik ermöglicht rasche Härtungszeiten bei Zimmertemperatur und in vielen Fällen können 100% Festgehaltssysteme für Härtung auf

diese Weise hergestellt werden, wodurch Lösungsmittelkosten und ecologische Probleme verringert werden. Ausserdem nehmen Elektron-Beschleuniger sehr wenig Platz ein, und Produktionsanlagen können innerhalb von wenigen Sekunden in Betrieb genommen werden. Angesichts des verhältnismässig niedrigen Energiebedarfs dieser Technik gehen alle Anzeichen dahin, dass vom wirtschaftlichen, ökologischen und Leistungsstandpunkt aus Elektron-Bündel-Härtung eine wichtige Rolle für die Härtung von Beschichtungsmitteln spielen wird.

Introduction

Refs. 1-3

Since the caveman started decorating his caves 25 000 years ago by mixing solid pigments with juices of animal and plant origin, the basic formulations of coatings have changed very little. Although types of paints have

changed, as well as techniques of use, the one characteristic that remains virtually unchanged is the use of a two-component system comprised of solids dispersed or dissolved in a suitable carrier, which is removed after the application of the coating, usually through a process of evaporation, to yield the desired finish.

The constant search by the coating industry for form-

*Paper presented at the South African Division Symposium held at Cape Town on 2-5 November 1978

ulations and techniques to enable the rapid curing of coatings, led to the development of highly volatile carriers (solvents) and the use of heat to accelerate the evaporation process. Living in a world that is daily becoming more conscious of the effects that modern technology can have on the ecology of the environment and the economic utilisation of its natural resources, the application of traditional coating systems and techniques have become subject to closer scrutiny. Highly volatile solvent systems are not only costly to manufacture, but can lead to serious pollution problems. Similarly, the use of heat in modern stoving tunnels is a good example of the uneconomic utilisation of limited energy resources. The electron-beam curing (EBC) of coatings represents a unique approach to overcome many of these problems.

For many years radiation power sources, such as gamma rays, electron beams and ultraviolet light, were little more than novelties to most processors—esoteric technologies valued for their unique capabilities in sterilising pre-packed medical devices, in the crosslinking of polyethylene for heat-shrinkable materials, and in the curing of coatings, inks and adhesives. These radiation techniques were not known for their economic viability in head-on comparisons with old-fashioned methods such as ethylene oxide in industrial medical sterilisation or heat in the curing of coatings. This is, however, no longer the case and the oil crisis of 1973 and the subsequent rocketing of costs in the petrochemical field has led to a new appraisal of radiation technology and what it can offer.

The relative importance of EBC in the field of radiation processing can be judged from the fact that of the almost 200 patents registered in the USA from 1972 to 1974, more than 34 per cent were related to the curing of coatings by means of electron accelerators¹. The past five years have witnessed the establishment of 16 EBC systems world-wide; mainly in Japan and the USA, with one processor each in the Netherlands, Germany and France, curing coatings on a variety of substrates such as timber, plastics and metal².

The question immediately arises why EBC has become such an attractive technique in the modern coatings industry. Briefly, the advantages of electron-beam curing of coatings can be summarised as follows³:

- higher line speeds are possible,
- less plant space is needed,
- solvent-free coating formulations are utilised, lessening solvent recovery and pollution problems,
- no catalyst residues are in the product,
- there is little heat damage to the substrate as the curing is effected at room temperature enabling a greater freedom in the choice of substrate material,
- a far better energy utilisation can be achieved through the use of EBC than with thermal curing, and
- the shorter production lines associated with EBC result in less start-up and shut-down waste than is the case with stoving tunnels.

These factors will be discussed in detail later in this paper.

Industrial electron accelerators

Ref. 4

The recent interest in the utilisation of EBC can, to a large extent, be ascribed to the development of very reliable electron accelerators in the past decade. This in turn led to a marked drop in radiation processing costs of nearly a hundredfold as compared to the earlier accelerators. The ease of handling of these machines and the high processing rates that can be achieved, to a large extent contributed to the establishment of EBC on an industrial level.

It falls beyond the scope of this paper to give more than a brief survey of the principles and variables associated with electron-accelerator processing. Electron accelerators of various designs are currently employed in the electron-beam curing of coatings and Figure 1 is a generalised description of such a machine.

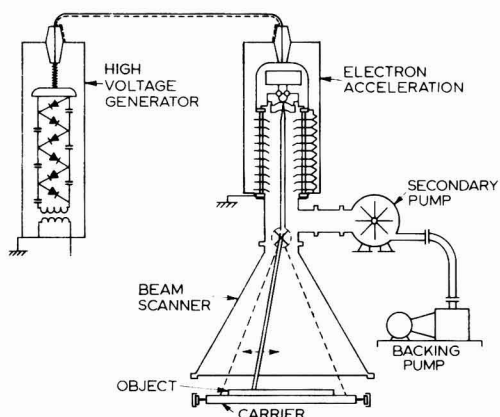


Figure 1. Schematic diagram of electron accelerator

High voltage generator: The on-line AC power supply is converted through a series of transformers and semiconductor rectifiers to a high-voltage DC power supply, which is housed in a metal tank filled with sulfur hexafluoride gas as an insulating medium.

Electron accelerator: The high-voltage power is transferred from the high-voltage generator (in some cases by means of a special hollow cable) to the electron accelerator. This accelerator consists of an evacuated acceleration tube contained in a metal tank filled with sulfur hexafluoride. Electrons emitted from a pure metal filament are focussed and enter the acceleration tube where they are accelerated to an energy corresponding to the high-voltage generator output-voltage. The acceleration tube is made from glass rings separated by metal electrodes. A uniform voltage gradient along the tube is achieved by a resistance column connected to the electrodes. The tube vacuum is maintained by a secondary ion pump and a primary rotary vacuum pump.

Beam scanner: After emerging from the acceleration tube, the electron beam enters the scanner where it is subjected to a varying magnetic field which causes the beam to

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Pity he didn't know about Proxel preservatives!

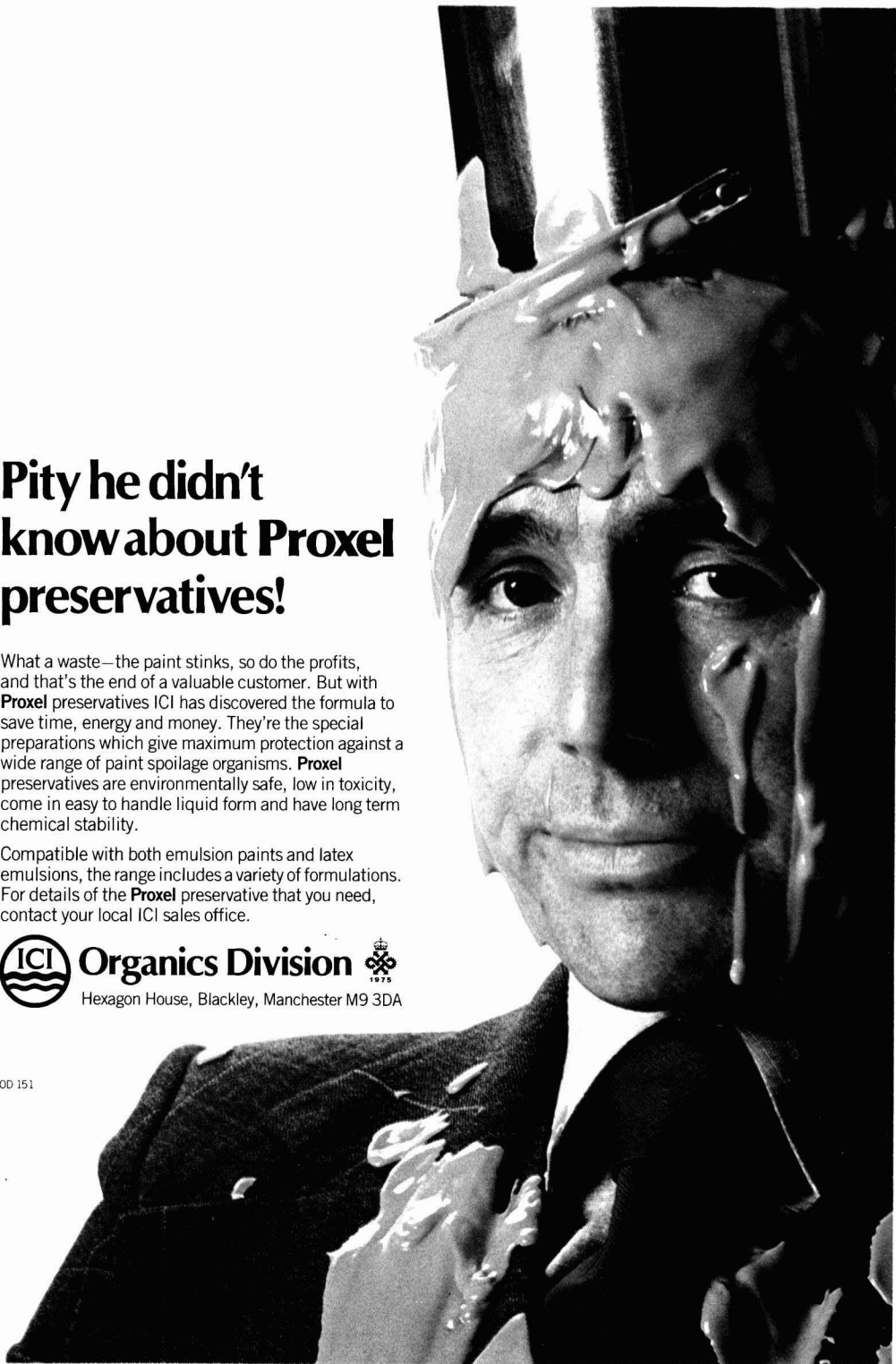
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sweep through an angle that can be varied*. The scanned beam passes through a very thin titanium-foil window which maintains the vacuum in the acceleration tube, and then falls on to the surface that has to be cured.

Coater and conveyor system: A variety of different coaters can be used to administer the desired coating which is then conveyed underneath the electron beam for curing. Curtain coating is more feasible at high speeds, whereas roll or spray coating may be used at lower speeds or viscosities.

Three parameters determine the processing capability of an accelerator:

Voltage: The accelerating voltage (terminal voltage) determines the depth to which the electron beam will penetrate a coating. The relationship of terminal voltage to useful penetration is shown in Figure 2 for materials of unit density. For materials having a density other than unity, the physical thickness of the coating must be multiplied by the density of the coating material in order to determine the effective thickness and terminal voltage required. In any material being irradiated by electrons, the radiation dose received at a given depth varies with both the electron energy and the material density. This effect is demonstrated in Figure 3 showing the variation with depth and energy in a material with unit density. The curves show dose versus penetration depth for various terminal voltages.

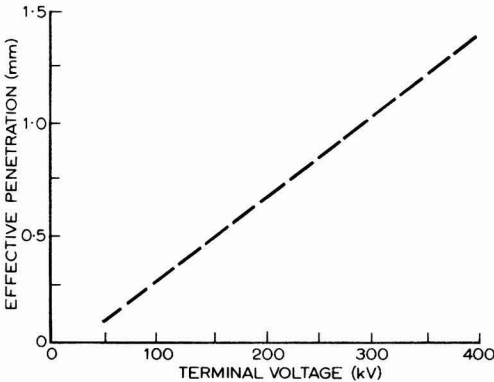


Figure 2. The effective penetration as a function of the terminal voltage in a coating of unit density

Actual electron energy at the surface to be cured will be lowered by the energy loss in the window foil and the air path.

Beam current: Beam current (i.e. the quantity of electrons per second) determines the output power of the accelerator in kilowatts, at a given accelerating voltage. Output power is defined as the product of beam current and accelerating voltage.

Required irradiation dose: Whilst the power output of an accelerator is expressed in kilowatts, the energy deposited in the coating is expressed in kilograys** (kGy), and referred to as the required absorbed dose to achieve complete curing of the coating.

*This beam can also be pulsed
 **1 Gy = 1 J/kg

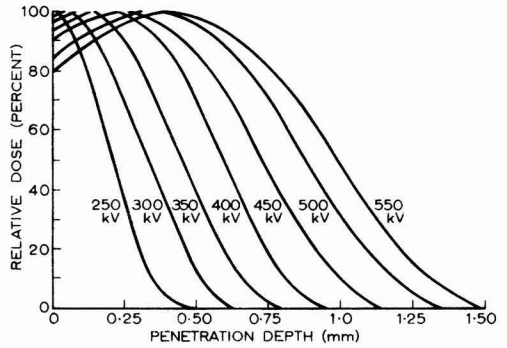


Figure 3. The relative absorbed irradiation dose as a function of the depth of penetration at different terminal voltages in a coating of unit density material

As stated earlier, EBC has the distinct advantage that very high processing rates can be achieved. Davison⁴ has calculated the output of some radiation curing arrangements. The theoretical output may be calculated from the equation:

$$R_{max} \cdot u = 1.45 \frac{E}{r_o} \frac{I}{W}$$

where

- R_{max} = the maximum dose in the coating (kGy)
- u = the linear speed of the coating line (m/s)
- E = the accelerating voltage
- r_o = the range of the electrons (g/m²)
- I = electron beam current (mA)
- W = the width of the coating line (m)

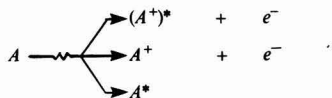
Davison warns, however, that this type of theoretical calculation must be carefully corrected for losses occurring at the accelerator window and backscattering in general. Line speeds of up to 200 m/min can be achieved, depending on the accelerator and the nature of the coating to be cured.

The chemical processes in radiation curing

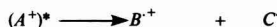
Refs. 5-11

It is important to consider how ionising radiation initiates chemical reactions⁵. Bearing in mind that chemical bond energies lie in the range of 1.5 to 8.5 eV, it is evident that energetic radiation, such as cobalt-60-gamma rays (1.15 MeV) or accelerated electrons (0.25 to 10 MeV), does not lead to the rupture of specific chemical bonds, as is the case with UV-light, but results in a less predictable pattern of bond scission.

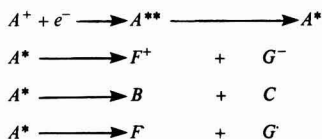
The interaction of energetic radiation with matter leads to the formation of positive ions and the associated energetic electrons, or to the formation of excited chemical species:



The electron resulting from the first ionisation of the molecule, can lead to secondary ionisations. If an excited ion possesses enough excitation energy, it can dissociate to form a radical ion and a radical:



Recapture processes can also take place and lead to the formation of excited molecules which may dissociate to yield secondary ions, molecular products and free radicals:



These chemically reactive radiolytic products can be trapped in the irradiated material or react to yield stable end products.

Effect of dose and dose rate

The formation of free radicals in an unsaturated coating system that is subjected to the energetic electrons from an accelerator, can initiate the curing of such a coating. This process can carry on until the curing is completed or the growth of the polymeric chains is seriously retarded by the increasing viscosity of the system. This gelation of the coating must, however, not be confused with the gel formation which takes place when a polymer is crosslinked. As a general rule, it may be stated that the degree of polymerisation or curing increases with an increase in irradiation dose. Various coating systems have, for economic reasons, been developed to lower the irradiation dose required to achieve complete curing of a coating.

In the case of EBC, not only is the polymerisation initiated by the energetic electrons, but the polymer so formed is also irradiated. This implies that great care has to be exercised in the choice of the coating system in EBC, as certain polymers can degrade under irradiation, whilst others predominantly undergo crosslinking. If the radiation degradation of the coating formed takes place, a point of equilibrium may be reached where the curing and degradation of the coating system counteract each other.

Because electron accelerators are capable of depositing energy at very high rates into a system (up to 2 MGy/min), it is essential to point out the effects that dose rate can have on the curing process. With a high-intensity electron beam, a very high local concentration of free radicals is formed in the coating. This results in an inefficient conversion of radiation energy to chemical energy because a large percentage of the free radicals recombine, instead of initiating the curing process. In practical terms, this implies that much higher radiation doses are required to achieve complete curing than would be the case at lower dose rates. This problem can be overcome by making use of several passes or by pulsing the electron beam, both methods resulting in effectively

lowering the dose rate of the electron beam and leading to higher energy utilisation.

Burland and Hirsch⁶ studied the effect of electron dose rate on the rate of disappearance of polyester double bonds in 65 per cent unsaturated polyester/35 per cent styrene solutions. They showed a linear increase in the rate of disappearance of polyester unsaturation with an increase in the dose rate up to about 200 kGy/min. At higher rates, this decrease in unsaturation levelled out and then decreased slightly up to 858 kGy/min (see Figure 4).

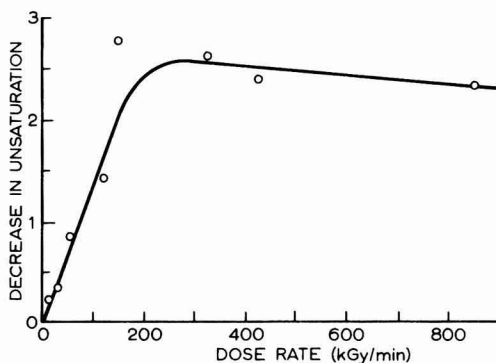


Figure 4. Rate of disappearance of polyester unsaturation as a function of dose rate

Radiation-curable coating systems

The following is a brief summary of the different coating systems currently being used on a commercial scale for EBC.

Unsaturated (polyester/vinyl monomer systems)

A large variety of different unsaturated polyester resins and vinyl monomers can be used for coatings in EBC. A list of such polyester resins⁷ is presented in Table 1.

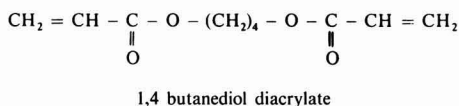
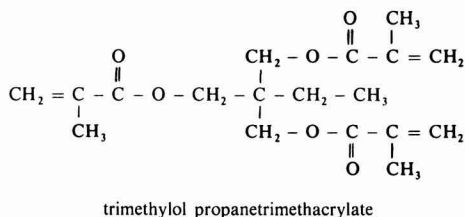
Table 1
Compositions for the manufacture of unsaturated polyesters for EBC

| Compositions | Mixing ratios |
|--------------|---------------|
| IP/MA/PG | 1/1/2 |
| PA/MA/PG | 1/1/2 |
| IP/FA/DEG | 2/1/3 |
| IP/MA/PG | 2/1/3 |

where IP : isophthalic acid
PA : phthalic anhydride
FA : fumaric acid
PG : propylene glycol
MA : maleic anhydride
DEG : diethylene glycol

The unsaturated polyesters formed by the mixtures in Table 1 can then be mixed with vinyl monomers such as styrene or vinyl acetate (10–30) in order to be cured by means of electron beams at absorbed radiation doses that range from 68 to 100 kGy. In order to sensitise the

coating system to radiation and to improve the quality of the coating, the above systems can be improved through the addition of polyfunctional monomers⁹. The latter class of additives includes the following compounds:

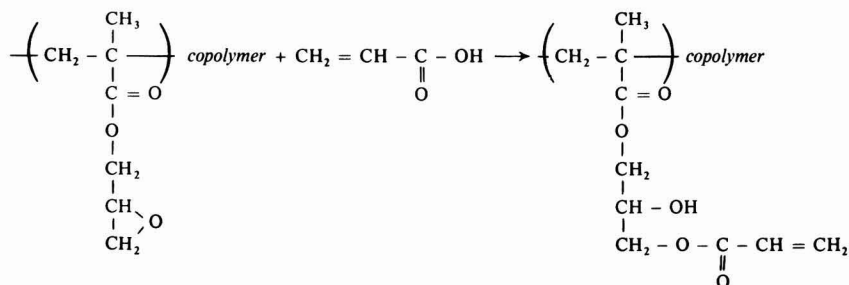


In the selection of these polyfunctional monomers⁹ the following guidelines are used:

- compatibility with the coating system
- ability to reduce the viscosity of the system
- radiation sensitivity
- ability to copolymerise with the pre-polymer
- low vapour pressure to limit evaporation losses
- the stability within the system before curing

Acrylic copolymer systems

The unsaturated-acrylic copolymer coatings¹⁰ can be prepared by the copolymerisation of glycidyl methacrylate with the desired comonomers to form an epoxy copolymer, followed by the reaction of the epoxy copolymer with acrylic acid.



Properties such as hardness, flexibility and solvent resistance of the cured coating are influenced to a large extent by the degree of unsaturation, and to a lesser extent by the comonomer composition. These acrylic coatings can be easily pigmented and applied by conventional procedures and equipment.

Other coating systems

A number of other coating systems are also used on a

limited scale including modified epoxy resins, poly(vinyl chloride) in the presence of additives, and polyethers that are modified to have terminal unsaturation.

Effect of oxygen on EBC

The "oxygen effect", the inhibition of curing by oxygen, can be a severely restrictive factor in the curing of certain coatings. Although a number of unsaturated polyester coating compositions can be cured satisfactorily in the presence of air, experiments carried out in the presence of nitrogen indicate that the irradiation dose required to achieve a proper cure can be reduced by almost 20 per cent in this inert atmosphere. For certain other coating systems this reduction can be as high as 500 per cent.

In many other instances, such as vinyl-monomer/oligomer coatings, oxygen present in air can inhibit the polymerisation process on the surface of the coating to render it tacky.

The above problems arise because oxygen is known to be an excellent free-radical scavenger. Because of the free-radical nature of the EBC process, oxygen can react with the chain-propagating free radicals to inhibit the curing process. Similarly, chain-scission of the polymer formed during the curing process is enhanced in the presence of oxygen.

Several methods¹¹ have been described to reduce the "oxygen effect":

- Blanketing the coating with an inert gas, e.g. nitrogen. For economic reasons, use is often made of an inert gaseous mixture (CO₂ + N₂) produced by the stoichiometrical combustion of petroleum gas.
- A foil of polyethylene terephthalate is often employed on an industrial scale in the manufacture of certain precured laminates.
- Elevated temperatures are sometimes used to decompose the peroxides formed during the curing process.
- Paraffin wax can be added in small quantities to the coating system. During the curing of the coating the wax diffuses on to the surface of the coating, forming a protective layer to exclude oxygen.
- High dose rates can also be employed to counteract the diffusion of oxygen into the coating during the curing process.

As a general rule, it is accepted that the oxygen level during EBC must be kept below a value of 0.05 per cent.

Advantages of electron-beam curing

Refs. 12, 13

From an industrial point of view, the economic gains to be reaped from using EBC are of prime importance. In order to demonstrate the most important differences between EBC and stoving, a comparison between these two techniques is presented in Table 2. This table relates to a survey¹² which was carried out in 1975 for a West German company manufacturing 2500 coated doors per day (1.55 million m²/year).

Table 2
A comparison between EBC and stoving, based on an annual production of 1.55 million m².

| Curing method | EBC | Stoving |
|---|-----------------------------|-----------------------------|
| Capital investment | \$ 875 000 | \$ 407 000 |
| Amortisation (5 years) + interest | 273 000 \$/a | 127 500 \$/a |
| Floor cost (including heating, lighting, ...) | 22 500 \$/a | 75 000 \$/a |
| Total costs function of time K_t | 295 500 \$/a | 202 500 \$/a |
| Labour and overhead costs | 161 500 \$/a | 161 500 \$/a |
| Power | 35 000 \$/a | 145 000 \$/a |
| Maintenance | 43 750 \$/a | 20 000 \$/a |
| Total costs function of quantities K_q | 240 250 \$/a | 326 500 \$/a |
| It is calculated that: | $K_t = 0.191 \text{ $/m}^2$ | $K_t = 0.131 \text{ $/m}^2$ |
| Raw material (coatings) | $K_q = 0.155 \text{ $/m}^2$ | $K_q = 0.211 \text{ $/m}^2$ |
| Solvent post-combustion | $K_m = 0.150 \text{ $/m}^2$ | $K_m = 0.200 \text{ $/m}^2$ |
| | $K_c = 0$ | $K_c = 0.020 \text{ $/m}^2$ |
| Production cost | 0.496 \$/m ² | 0.562 \$/m ² |

From the above table the following inferences can be made:

- A saving of 11 per m² in the overall production costs can be achieved. Corresponding figures of up to 40 per cent have been reported in other surveys.
- There is a more efficient use of power. If an accelerator is compared to an oven, savings of up to 2000 per cent can be achieved, but it has to be appreciated that this applies only to a small part of the overall energy consumption.
- Less plant space is required.

Although labour costs for both EBC and stoving are taken to be the same in Table 2, EBC lends itself to a higher degree of automation and some consider this to be only 20 per cent of that of conventional stoving¹³.

In addition to the above mentioned advantages of EBC, the following benefits are also obtained:

- Complete curing of coatings can be achieved in a matter of seconds.
- Treatment can be carried out at room temperature,

therefore, EBC is suitable for temperature sensitive substrates, e.g. plastics, wood and paper.

- Superior coating qualities can be obtained with excellent finishes.
- Better adherence of coatings to certain substrates, through radiation grafting of the coating to the substrate, can be obtained.
- Start-up and shut-down waste in EBC can be as low as 5 per cent compared to values of 30 per cent in the case of stoving.
- The solvent-free coating formulations used in EBC, imply that very little air and water pollution

is associated with this technique. In stoving, up to 50 per cent (on a mass basis) of the coating composition will be released into the atmosphere. For the production rates stated in Table 2, about 750 kg out of the initial 1600 kg of coating will be released as solvents.

Disadvantages of electron-beam curing

Among the disadvantages of this process are the following:

- As shown in Table 2, the initial capital investment for this process can be relatively high.
- New coating compositions are required as conventional paints do not, in general, cure upon irradiation.
- The coating compositions required for EBC are usually very viscous, and there are engineering problems of application at very high conveyor speeds.
- Inert atmospheres are generally required for efficient surface curing.

- Evaporation of reactive components from the coating mixture must be controlled, since final coating properties and process economics will be significantly affected.
- The process is most efficiently adapted to flat surfaces.
- The large amounts of ozone generated could be a health problem if not handled correctly.

Conclusions

EBC has established itself in the coating industry as an economically viable process. This process lends itself well to a better utilisation of limited energy and raw material resources. As a consequence, this new technology is associated with the limited impact which it has on the pollution of the environment and its excellent performance. It can be expected that this technology will play an increasing role in the coating industry in future.

[Received 6 February 1979]

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Modern developments in aqueous industrial coatings*

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Summary

This paper reviews three recent developments in aqueous industrial coatings. The first part deals with a comparison of two types of aqueous polymeric paint binders, both containing a common monomer, viz. the vinyl ester of an alpha-alpha-branched chain synthetic carboxylic acid ("VeoVa" 10). The two polymeric paint binders were prepared by two entirely different routes, (1) the commonly used emulsion copolymerisation, with vinyl acetate as the principal comonomer, and (2) a bulk polymerisation process where comonomers included styrene butyl acrylate and hydroxyethyl methacrylate.

In the second part, the development of epoxy resin based binders for electrodeposition paints with high corrosion resistance is described. Further improvement in the corrosion resistance of

epoxy ester based electrodeposition primers on bare steel has been sought and recent work has been directed at gaining a fuller understanding of the factors governing this. As a result of this work, improved anodic electrodeposition binders have been prepared according to the "high hydroxyl" principle. This principle has also been shown to be valid for cathodic electrodeposition binders.

The third section of the paper describes the present situation and the most recent developments in the field of water dispersible ambient temperature curing epoxy resin systems. The formulation of special epoxy resins, which readily emulsify in water, such as "Epikote" 255, and their application in the general maintenance coating field is reviewed.

Keywords

Types and classes of coatings and allied products

emulsion paint
electrocoating

Raw materials for coatings binders (resins, etc.)

latex
epoxy resin

Développements récents dans le domaine de revêtements industriels à base d'eau

Résumé

Dans cet exposé l'auteur passe en revue trois développements récents dans le domaine de revêtements industriels à base d'eau. La première partie comprend une comparaison de deux types de liants polymères pour peintures à base d'eau, contenant le même monomère, c'est-à-dire, l'ester vinylique d'une acide carboxylique synthétique avec un branchement alpha-alpha ("VeoVa" 10). Les deux types de liants polymères ont été préparés par deux méthodes différentes: (1) Le procédé de copolymérisation en émulsion, très souvent utilisé, où l'acétate de vinyle est le comonomère principal, et (2) un procédé de polymérisation en masse où le styrène, l'acrylate de butyle et le méthacrylate d'hydroxyéthyle sont compris parmi les comonomères.

Dans la deuxième partie, on décrit la mise au point des liants à base des résines époxydes pour peintures destinées à être appliquées par électrodéposition et ayant une résistance élevée à la corrosion. On cherche une autre augmentation de la résistance à

la corrosion des peintures primaires à base des résines époxydes pour électrodéposition à l'acier nu, et les études récentes ont été visées sur l'obtention d'une compréhension plus profonde des facteurs qui exercent une influence à cet égard. En raison de ces études, on a préparé, selon le principe de "hydroxyl élevé", des liants anodiques supérieurs pour électrodéposition. On a démontré d'ailleurs que ce principe est valable dans le cas des liants cathodiques pour électrodéposition.

Dans la troisième partie on décrit, à la fois, la situation actuelle et les développements récents dans le domaine des systèmes époxydes dispersibles à l'eau et qui peuvent être durcis à la température ambiante. On passe en revue également la mise au point des résines époxydes spéciales, qui s'émulsifient très facilement dans l'eau, tels que l'"Epikote" 255, et leur application dans le domaine des peintures d'entretien générale.

Moderne Entwicklungen auf dem Gebiet von wassergetragenen Industrielacken

Zusammenfassung

In dieser Abhandlung werden drei kürzliche Neuentwicklungen von Industrielacken auf Wasserbasis besprochen. Der erste Teil befasst sich mit dem Vergleich von zwei Typs wässriger, polymerer Lackbindemittel, wobei beide das gleiche Monomer enthalten und zwar den Vinylester einer alpha-alpha verzweigten Kette synthetischer Monokarbonsäure ("VeoVa" 10). Die zwei polymeren Lackbindemittel wurden auf zwei gänzlich verschiedenen Wegen hergestellt (1) der allgemein benutzten

Emulsionspolymerisation mit Vinylacetat als das hauptsächlichste Komonomer und (2) einem Massenpolymerisationsverfahren, welche die Komonomere Styrolbutylakrylat und Hydroxyäthylmethakrylat einschlossen.

Im zweiten Teil wird die Entwicklung von Bindemitteln für Elektrophoreselacke hoher Korrosionsbeständigkeit beschrieben. Nach weiterer Verbesserung bezüglich Widerstand

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genen Korrosion direkt auf Stahl mittels Elektrophoreseprimer auf Basis von Epoxyestern wurde gesucht, und neuere Arbeiten wurden darauf gerichtet, ein besseres Verständnis für die Faktoren zu gewinnen, von denen dies abhängig ist. Als Ergebnis dieser Arbeit wurden verbesserte anodische Elektrophoresebindemittel hergestellt entsprechend dem "hohen Hydroxyl" Prinzip. Dieses Prinzip erwies sich auch als gültig für kathodische Elektrophorese-Bindemittel.

Introduction

Refs. 1, 2

There is no doubt that aqueous industrial coatings nowadays play an important role in the coating industry. They belong to the class of coatings which are probably best characterised by the German word "umweltfreundlich", i.e. friendly to the environment. Powder coatings, high solids coatings and radiation curing systems are amongst the alternative "umweltfreundliche" systems.

An increasing amount of data¹ on the relative market importance of aqueous coatings is becoming available. Figure 1 shows how the market share of the water thinnable coatings in the USA has increased over the past years and how it is expected to change in the near future. Recently, a study of trends in European industry yielded similar indications: aqueous systems at present constituting some 10 per cent of the total industrial coatings market, and expected to grow to about 25 per cent in the next ten years. In certain specific areas (domestic appliances, industrial maintenance) they already hold 15 per cent or more of the market (automotive primers), in other areas (can coating) more spectacular growth is expected in the immediate future.

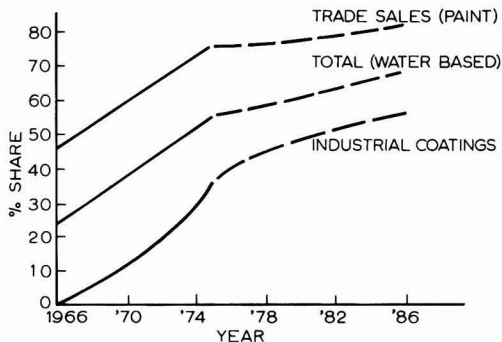


Figure 1. Growth of water based coatings expressed as market share in the paint industry of USA.

In aqueous coatings many publications set the scene by attempting to define various classes of systems. A recent article², which included the views of nine major German paint industries, however, showed that the definition of aqueous coatings still shows appreciably different interpretation, and refers to this situation as a "Babylonian confusion of tongues". Probably no truly exact distinctions can ever be made. All such systems can be considered as colloidal systems, which differ in optical properties due to particle size variations or differences in the refractive indices of the disperse and homogeneous phases. Most commonly a division is made in practice between (a) water soluble coatings and (b) aqueous

Der dritte Teil der Abhandlung beschreibt die augenblickliche Lage und die allerneuesten Entwicklungen auf dem Gebiete der bei Zimmertemperatur härtenden wasserdispergierbaren Epoxyharzsysteme. Überblickt wird ebenfalls die Rezeptierung spezieller Epoxyharze, welche leicht in Wasser emulsifiziert werden können, wie z.B. "Epikote" 255, und deren Anwendung auf dem Gebiete des allgemeinen Instandhaltungsanstrichs.

dispersions/emulsions. For convenience, this division is accepted.

Water soluble coatings, then, are those systems based on solutions which are transparent blends of water and resin vehicles and which remain clear on further dilution with water. These solutions do not contain surface active agents and/or protective colloids to provide stability, as is the case with dispersions/emulsions. Their water compatibility is due to the presence of built-in polar groups, mainly carboxyl groups. After neutralisation with amines the systems become water soluble. This means that on addition of water, micelle-type particles are formed, which are sufficiently small in diameter to yield clear solutions. This clarity and phase homogeneity, particularly at low vehicle concentrations, can be improved by the addition of polar solvents at such concentrations that the system remains non-inflammable.

Similarly, an aqueous dispersion is defined as a fine dispersion of a polymeric binder in water, and an emulsion is defined as a fine dispersion of a liquid resin in water. An aqueous dispersion is very often referred to as a latex and is usually prepared by an emulsion polymerisation procedure, which means polymerisation of water/monomer(s) emulsion in the presence of initiators and surface active agents and often protective colloids. Aqueous dispersions can, however, also be prepared by post-dispersion in water of polymeric species which have been polymerised in some other way. In this case they are referred to as "AD" (a real Aqueous Dispersion) to distinguish between them and the latex type of dispersion.

This paper will deal first with development work carried out on thermosetting reactive latices and "AD's" prepared by post-dispersion of bulk polymers. Secondly, heat cured water soluble epoxy resin esters will be discussed and, finally, cold curing two-pack epoxy resin emulsions will be described.

Reactive latices and "AD's"

Ref. 3

The binders considered in this section contain a common monomer, which is the vinyl ester of an alpha-alpha branched chain synthetic carboxylic acid, further referred to as "VeoVa" 10. Systems of both types mentioned above have been studied, i.e.

- Latices basically composed of a vinyl acetate/"VeoVa" 10 copolymer backbone, and containing some pendant reactive amide and carboxyl groups.
- An aqueous dispersion, "an AD" prepared by a special post-dispersion of a bulk polymer based on "VeoVa" 10, styrene, hydroxyethylmethacrylate and butyl acrylate.

Reactive latices, as such, are certainly not novel; large quantities are already used in the textile industry. More recently, however, they have been given more attention by the coatings industry. For the present comparison a relatively simple type of latex has been selected, partly with a view to the economics of such a product. The monomer composition is given in Table 1.

Table 1
Monomer composition (%w) of
reactive latices tested

| Type Reference No. | Standard 1 | MMA 2 |
|-----------------------------|---------------|----------|
| Vinyl acetate "Veova" 10 | (VA) 70 25 | 60 25 |
| Methyl methacrylate | (MMA) — | 10 |
| Acrylamide | 3 | 3 |
| Acrylic acid | (AA) 2 | 2 |

Details of the preparation are given in Table 2.

Table 2
Preparation of a reactive latex on a 5-1 scale
Composition: VA/"Veova" 10/MMA/acrylamide/AA 60/25/10/3/2

| Components | | PBW | % |
|-------------------------|--|-----------------|----------------|
| Reactor charge | water | 1385 | 33.06 |
| | Abex VA 50 | 92.4 | 2.21 |
| | K ₂ S ₂ O ₈ | 4.62 | 0.11 |
| Monomer emulsion | water | 619.0 | 14.79 |
| | Abex VA 50 | 110.8 | 2.65 |
| | K ₂ CO ₃ | 4.62 | 0.11 |
| | acrylamide | 55.5 | 1.33 |
| | acrylic acid | 37.1 | 0.89 |
| | Vinyl acetate "Veova" 10 | 1108.8 462.0 | 26.49 11.04 |
| | Methyl methacrylate | 184.8 | 4.41 |
| initiator | H ₂ O | 115.5 | 2.76 |
| | K ₂ S ₂ O ₈ | 2.36 | 0.06 |
| chain transfer agent | dodecyl mercaptan | 3.68 | 0.09 |
| | Solids content, | %w | 45.3 |
| | pH | | 4.1 |
| | Viscosity at 23°C. | P | 10.3 |
| | Particle size, | μm | 0.07-0.09 |
| | Conversion, | % | 99.6 |

The initial reactor charge is heated under nitrogen while the monomer pre-emulsion is prepared by adding the monomer mixture to the agitated aqueous phase. As soon as the temperature of the reactor charge reaches 72°C, addition is commenced of the monomer pre-emulsion and the initiator solution in two streams. The temperature is allowed to rise to 78-80°C and the addition is continued. The rate of addition should be such that addition of the monomer pre-emulsion is completed at the end of 3.5 hours and the addition of the initiator solution continues for a further 20-30 minutes into the subsequent digestion period. The chain transfer agent is added after 15 per cent of the monomer emulsion has been added to the reactor charge. During the digestion period of two hours, the temperature is maintained at 80 ± 1°C. The latex is then cooled and filtered.

Post-dispersions of polymers in water are less well known at present. Recent work³ on mass polymerisation of "Veova"-containing products has shown that polymeric binders of a very interesting design can be prepared in this way. The technique involves copolymerisation of various monomers in the absence of solvents at a fairly high temperature (170°C). Under these conditions the differences in reactivity of such monomers as styrene and the vinyl ester type monomer "Veova" 10 is no obstacle to a true copolymerisation. The lowest reactivity monomer is precharged and the other more reactive comonomers are added gradually at the reaction temperature over about five hours.

The bulk polymer used in the present comparison had a monomer composition as shown in Table 3.

Table 3
Monomer composition
of the mass polymer
used in the "AD"

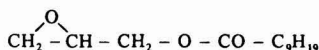
| Type of monomer | Amount, %w |
|-------------------------------|---------------|
| "Veova" 10 | 36.4 |
| Styrene | 29.2 |
| Hydroxyethyl- methacrylate | 17.7 |
| Butyl acrylate | 16.7 |

In the initial experiments, certain amounts of methacrylic acid were used in addition to provide the necessary degree of hydrophilicity in the polymer. Polymer viscosities, however, became inconveniently high with negative effects both on the polymerisation process and the dispersion characteristics. Therefore, reaction of hydroxyl group containing polymers with anhydrides to yield mono-esters was studied as a means of rendering the binders water soluble.

By coincidence and rather surprisingly, it was found that a polyester type adduct of 1 mole trimellitic anhydride (TMA) and 1.04 mole of a glycidyl ester* of the same branched acid which forms the basis of "Veova" 10, is very suitable for this purpose. This adduct reacts with hydroxyl-rich resins by transesterification: the polyester is cleaved and bound to the hydroxyl-rich backbone, thereby introducing COOH-groups and rendering the adduct readily water-dispersible, without the need of additional surfactants. The nature of this reaction is shown in Fig. 2. The amount of adduct required was 15.6 parts per hundred parts of polymer by weight, and the transesterification conditions were 30 minutes at 135°C.

White paints were made from the reactive latices and the AD (further referred to as LR-2047) using titanium dioxide at a pigment/binder ratio of 0.7. A hexamethoxymethyl melamine (HMMM) type of resin was used in a ratio of 85/15 w/w polymer/HMMM as the curing agent. Systems were applied by spraying on to bonderised steel and on to primed bonderised steel (B 125) and stoved for half an hour at 150°C after a flash-off for 30 minutes. Details of the paint formulations

*"Cardura" E 10, the glycidyl ester of an α-branched saturated fatty acid having 10 carbon atoms:



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are given in Tables 4 and 5 and details of the properties assessed are given in Table 6.

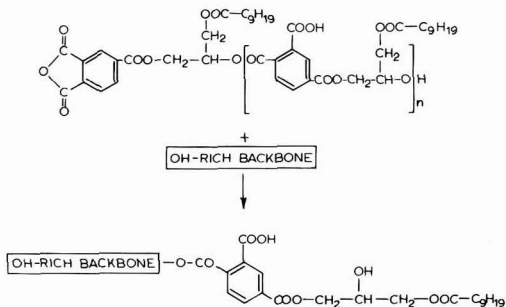


Figure 2. Reaction of a polyester type adduct of TMA/Cardura E10 with an OH-rich backbone.

Table 4
Paint formulation for reactive "Veova" 10 based latex

| Composition | Parts by weight |
|---|--|
| 30% latex solution, neutralised with 2-amino-2-methylpropanol to pH 7.0 | 381.0 |
| 35% Cymel 301 in H ₂ O/IPA ¹ 2:1 | 61.2 |
| 35% "Cardura" LR 28 in water, neutralised with dimethyl ethanol amine | 20.4 |
| Pigment, Tioxide R-CR3 | 100 |
| Defoamer, Bevaloid 677 ² | 0.2 |
| Surface active agent BYK 301 ³ | 0.0069 |
| Catalyst Anchor S 475 ⁴ | 2.13 |
| AMP (2-amino-2-methylpropanol) ⁵ | to adjust pH to 8.0 |
| water | to adjust viscosity to 25 cup 4 (Ford) |

Paint characteristics

| | |
|---|---------|
| Latex polymer/LR 28/Cymel 303, solids ratio | 80/5/15 |
| Pigment/binder ratio | 0.7 |
| Bevaloid 0.2 %w on pigment | |
| BYK 301 0.02 %w on solids | |
| S 475 1.5 %w on binder | |

Paint preparation:

Pigment, part of the 30% latex solution (to pigment/binder ratio 3.0), Bevaloid and enough water to give a smooth paste are ball-milled for 24 hours. This paste is added to the remaining 30% latex solution under stirring, followed by the other ingredients in the above sequence.

¹IPA = isopropyl alcohol

²Ex. Bevaloid Ltd

³Ex. BYK-Mallinckrodt

⁴Ex. Anchor Chemicals

⁵Ex. IMC Chemie GmbH (West Germany)

Table 5
Paint formulation with "Veova" bulk polymer LR 2047

| Composition | Parts by weight |
|---|---|
| 50% aqueous dispersion of LR 2047, "neutralised" with 2-amino-2-methylpropanol (0.9 eq/eq COOH) | 242.9 |
| Cymel 301 | 21.38 |
| Tioxide R-CR3 | 100 |
| water | to adjust viscosity to 15 secs Ford cup 4 |

Paint characteristics

| | |
|--------------------------------------|-------|
| Mass polymer/Cymel 303, solids ratio | 85/15 |
| Pigment/binder ratio | 0.7 |

Paint preparation:

Aqueous dispersion, Cymel 303, pigment and enough water to give a smooth paste are ball-milled for 48 hours. Subsequently, the paste is diluted with water to the desired spraying viscosity.

From these results, it is apparent that white aqueous stoving paints based on both the latex binders and the AD (LR 2047) have interesting combinations of properties. The LR 2047 based paint is generally somewhat superior in chemical resistance and appearance (flow and image clarity). The latex based paint films tend to be somewhat harder. Formulation variations in terms of MF-resin type, level and type of neutralisation agents have been shown to result in slight improvements in certain particular aspects.

A single answer to the question, "is a latex concept better than an AD?" cannot be given, as both systems have advantages and disadvantages. In order to give some idea on the relative merits of these systems they can be compared in two stages: (a) Differences in preparation, latex/dispersion and paint characteristics, and (b) Comparison of performance of the cured coating.

The more important aspects of preparation and paint characteristics of the two paints are compared in Table 7.

It is to be expected that polymers prepared by completely different routes will have different properties, particularly because the constraints of both routes lead, when optimising, to polymers of a different composition. As discussed before, the new bulk polymerisation process enables true copolymerisation of monomers with widely varying reactivities, thereby providing much greater freedom in monomer composition than is possible with the emulsion process.

This latter process, however, can be carried out at much lower temperatures and can, therefore, result in polymers with much higher molecular weights, and requiring less reactive sites for crosslinking.

The choice of a given technique will, in practice, depend on the end-use requirements. The data collected here may help in making this choice.

Table 6
 Film properties of the reactive latex and LR 2047 based paints

| Property | Substrate | Performance of white pigmented stoving paints based on: | | |
|--------------------------|-------------|---|-----------------|-----------------|
| | | Latex 1 incl. MMA | Latex 2 no MMA | "AD" LR 2047 |
| Thickness, μm | | 37 | 40 | 30 |
| Gloss 45°, % | B 125 | 68 | 84 | 83 |
| | B 125 + pr. | 76 | 86 | 86 |
| Hardness | | | | |
| Buchholz | B 125 | 113 | 96 | — |
| König | B 125 | 189 | 157 | 161 |
| Impact, | | | | |
| reverse, | in lbs | | | |
| | steel | 2 PF | 20 PF | 15 |
| | steel + pr. | 2 F | 5 P | 1 |
| direct | steel | 20 PF | 55 P | 25 |
| | steel + pr. | 10 P | 30 P | 12 |
| Erichsen penetration, | mm | 8 | 8 | 6.7 |
| Mandrel bend, | inch | 6.8 | 6.3 | 5.5 |
| | steel | $\frac{1}{8}$ P | $\frac{1}{8}$ P | $\frac{1}{8}$ F |
| | steel + pr. | $\frac{1}{8}$ PF | $\frac{1}{8}$ P | $\frac{1}{8}$ F |
| Adhesion (crosshatch) | steel | Gt 0 | Gt 0 | Gt 0 |
| | steel + pr. | Gt 0 | Gt 0 | Gt 0 |
| Xylene, | s | 90 | 60 | 90 |
| MIBK | B 125 | 60 | 60 | 225 |
| Detergent, | | | | |
| blisters | 24 h 80°C | | | |
| gloss | B 125 | t.l.a. | t.l.a. | OK |
| blisters | B 125 | — | — | 87 |
| | B 125 + pr. | OK | OK | — |
| Humidity, | | | | |
| blisters | DEF 1053 | | | |
| blisters | B 125 | 8 D | 8 D | OK |
| gloss | B 125 + pr. | OK | OK | |
| | B 125 + pr. | 76 | 85 | |
| Salt-spray, | | | | |
| blisters | ASTM | | | |
| creep, | mm | OK | 4 D | OK |
| blisters | B 125 | 1-2 | t.l.a. | none |
| creep, | mm | OK | OK | OK |
| | B 125 + pr. | 0.5-1.5 | 0-0.5 | none |

Formulation: 85/15 polymer/HMMM, neutralised to 0.9 with AMP, stoved 30 min/150°C P/B 0.7.
 B 125 = Bonder
 pr. = primer
 MIBK = Methyl isobutyl ketone

Heat cured water soluble epoxy resin esters

Ref. 4

From the start, water soluble epoxy resin esters were amongst the most commercially important resin binders for the automotive industry. This began as soon as electrodeposition (E/D) got a foothold as a very suitable means of applying these systems and has continued to the present day.

The E/D process is now fully established in the automotive industry and in addition to water soluble epoxy esters, maleinised natural oils and acidic alkyd resins have found acceptance. In the early 1970's binders based on maleinised polybutadiene oil (LMPB's—low molecular weight polybutadiene) also came into industrial use, particularly in W. Europe. The progress of these systems was due to one key advantage: their good corrosion resistance when applied to non-phosphated steel substrates.

This property is important in modern automotive applications, since most cars now used in W. Europe are of the integral chassis type where spray phosphating always leads to some poorly, or incompletely phosphated areas. Primers offering good corrosion protection on poorly phosphated steel are thus quite essential for ensuring that modern cars have a long service life. The superior performance of LMPB's in this respect was ascribed to the low water permeability of polybutadiene films⁴.

The author's more recent work, however, has thrown a different light on this view.

A more fundamental study of electrodeposition systems was initiated in order to find a way of formulating epoxy resin E/D binders with improved corrosion resistance on bare steel, to meet the improved standards set by the LMPB-based materials.

In the first instance, typical representatives of the epoxy

Table 7
Aspects of binder preparation and paint characteristics
of a reactive latex and an "AD" based system

| Type of binder | Reactive latex | "AD", aqueous disp. |
|---|----------------------------|---------------------|
| <i>Preparation</i> | | |
| Type of polymerisation | emulsion | mass (bulk) |
| Commercial experience | large | little |
| Reaction conditions | | |
| – temperature | medium | high |
| – temp. accuracy | narrow | fairly wide |
| – viscosity of mixture | low | high |
| Reaction feed mixture | complex | simple |
| Choice of monomers | limited | wide |
| Particle size control | easy | difficult |
| Dispersion | in situ | separate process |
| <i>Latex/dispersion characteristics</i> | | |
| Particle size | variable | ~90 nm (900 Å) |
| Molecular weight, \bar{M}_w | 150 000 | 20 000 |
| Stabiliser | external | built-in |
| Stability of dispersion | excellent | mediocre |
| <i>Paint characteristics</i> | | |
| Organic solvent content, %w | 2 | 2 |
| Additives required for: | | |
| | cure rate | – |
| | mar resistance | – |
| | flash rusting | – |
| Viscosity for spray | 22 s Ford cup 4 | 14 s Ford cup 4 |
| Solids content, %w | 40 | 60 |
| <i>Film properties</i> | | |
| Solvent resistance | moderate | moderate/good |
| Detergent/humidity resistance | moderate, with primer good | excellent |
| Salt-spray resistance | good | excellent |

and LMPB binder systems were chosen, viz. "Epikote" binder LR-38, a maleinised modified long-oil ester, and a commercial binder based on an LMPB.

Clear films were applied to bare steel and bonderised steel panels by electrodeposition and, after stoving, the panels were subjected to salt-spray testing. It was confirmed that the LMPB-based binder gave much better performance on bare steel than the "Epikote" binder. On bonderised steel, however, both systems were equal.

It was then questioned whether the disappointing performance of the "Epikote" LR-38 system could be associated with the method of application, the aqueous phase, the presence of free fatty acids in the binder or, possibly, some detrimental effect of the maleinisation. These aspects were examined in various tests; spray application instead of E/D, use of solvent instead of water, removal of free fatty acids and omission of the maleinisation. None of these changes led to noticeable improvements in the level of corrosion resistance.

The poor resistance of the LR-38 films manifested itself in the salt-spray cabinet by a rapid total loss of adhesion followed by rust formation. The loss of adhesion started on both sides of the scratch and was obviously promoted by the NaOH formed at the film/metal interface as a result of electrochemical corrosion processes. The fact that on bonderised steel the corrosion resistance was found to be much greater, is explained by the higher electrical resistance of the phosphate layer which suppresses these electrochemical reactions and thus the NaOH formation.

It was then assumed that the differences in performance between "Epikote" LR-38 and the LMPB based system on bare steel were caused by a difference in the NaOH resistance of the adhesion promoting groups present in the films: "Epikote" LR-38 mainly contains carboxyl groups, whereas the LMPB based system also contains the more alkali resistant OH-groups.

The validity of the latter assumption was borne out by the following results:

- (1) The cure at 180°C of films based on an LMPB leads to the formation of a substantial number of OH groups (determined by IR spectroscopy). These films were found to have a very high salt-spray resistance.
- (2) Curing of the same LMPB based system at room temperature with conventional paint driers (0.1 per cent w Pb + 0.02 per cent w Co) yields films with a high OH-content and a high salt-spray resistance; in the absence of paint drier, films with much lower OH content and considerably lower salt-spray resistance were obtained.
- (3) Combinations of "Epikote" 1007 with low amounts (1 per cent w or 5 per cent w) of hexamethoxymethyl melamine (HMMM) gave, after cure at 180°C, films with a relatively high (calculated) OH content and a very high salt-spray resistance. Combinations with higher amounts of HMMM (15 per cent w and 25 per cent w) gave films with a low OH content and a very low corrosion resistance.

Very low amounts of HMMM, such as 1 per cent w, however, give films with poor mechanical properties and for that reason at least 5 per cent w should be used. As the HMMM reacts with the epoxy resin without any self-condensation, it is possible to calculate the OH-content in the final film and so determine the value which offers the desired level of corrosion resistance. This value appears to be in the range of 200–400 meq OH/100 g.

Despite these findings, not all hydroxyl-rich binders have good salt-spray resistance. For instance, poor corrosion resistance was displayed by hydroxyl-rich films based on polyester type resins. This is most probably related to the fact that these resins are generally more susceptible to hydrolysis than epoxy based systems because of the presence of the weaker ester bonds.

Summarising, the general design of new "Epikote" electrodeposition binders, having excellent corrosion resistance on bare steel, should be based on the following considerations:

–The preparation of materials with hydroxyl-rich backbones based on "Epikote" resins.

–The reaction of this backbone with cyclic anhydrides to obtain the desired water solubility characteristics.

–The combination of these binders with small amounts of curing resins (e.g. melamine resins) to provide a sufficient degree of crosslinking and at the same time a sufficiently high level of hydroxyl groups (200–400 meq. OH/100 g cured film).

Following this general design* a number of epoxy resin binders have been formulated using the following approach:

Terminal hydroxyl groups were introduced into a solid epoxy resin ("Epikote" types 1001 or 1004) by reacting the epoxy groups with stoichiometric quantities of hydroxy acids, such as lactic or, preferably, dimethylol propionic acid (DMPA). The resulting hydroxyl-rich "backbones" (8–12 OH groups/molecule) were then

reacted with a cyclic anhydride such as succinic or trimellitic anhydride (TMA), to introduce the carboxyl groups necessary for solubilisation in water.

It soon became clear that these oil-free binders were too "hard", i.e. when applied by E/D they flowed poorly during the actual deposition step and consequently formed rough, poor-looking coatings. Better flowing binders were obtained by replacing the simple cyclic anhydrides with substituted succinic anhydrides in the form of pre-maleinised fatty acids. Unfortunately, however, this approach always led to disappointing salt-spray ratings, a fact possibly caused by steric factors.

It was then discovered that a similar flow-improving effect resulted, without much influence on salt-spray resistance, when "Cardura" E10 was incorporated into the binders, as described in the previous section. Binders of this type, in combination with small amounts of melamine or phenolic resins as crosslinkers, have good E/D behaviour, good mechanical properties, and a salt-spray resistance comparable to that of commercial LMPB systems. The trimellitic anhydride/"Cardura" E10 (TMA/CE 10) combination used led to an especially high bath stability, and this binder was, therefore, selected for sampling to customers under the code LR 2052. Customer reactions so far have been quite positive and the expectations regarding the high salt-spray resistance of this binder on non-phosphated steel have been fully confirmed.

With a view to lowering the raw material costs (the dimethylol propionic acid used in binder LR 2052 being rather expensive), another OH rich binder was developed, LR 2053. This system is based on a linear backbone containing "Epikote" 828, diphenylolpropane, adipic acid and "Cardura" E10 and again is rendered water soluble with a TMA/CE 10 combination. This binder performs as well as LR 2052, with an only marginally lower salt-spray resistance.

Some details on composition and performance of both these binders are given in Table 8.

Table 8
Some details on composition and performance of
"high-hydroxyl" E/D Anodic "Epikote" ester binders

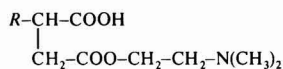
| Binder | LR 2052 | | LR 2053 | | Reference |
|--|------------|-----------|---------------|-------|---------------|
| | weight | moles | weight | moles | |
| <i>Composition</i> | | | | | |
| "Epikote" 828 | — | — | 32.0 | 3 | self-curing |
| "Epikote" 1001 | 57.1 | 2 | — | — | binder |
| Adipic Acid | 4.3 | 1 | 8.4 | 2 | based on |
| Dimethylol propionic acid | 8.0 | 2 | — | — | a maleinised |
| Diphenylol propane | — | — | 13.0 | 2 | LMPB + |
| "Cardura" E 10 | 17.5 | 2.4 | 32.9 | 4.5 | a phenolic |
| Trimellitic anhydride | 13.1 | 2.3 | 13.7 | 2.6 | type of resin |
| <i>Performance in an E/D primer, grey inactive pigmentation</i> | | | | | |
| <i>P/B 0.28, 25 µm films, epoxy ester/HMMM 95/5, stoved 30 min/180°C</i> | | | | | |
| E/D behaviour | | good | good | good | |
| Bath stability | | | | | |
| 40°C, | 10 days | very good | very good | good | good |
| Mechanical properties | | good | good | fair | |
| Salt-spray resistance | | | slightly less | | |
| on degreased steel | | good | than LR 2052 | good | |
| OH-content in film, | meq./100 g | ≈ 400 | ≈ 200 | — | |

*Formulations described are covered by the German Patent Application OLS 2700537, and other applications in a number of countries.

Cathodic E/D binders*

Ref. 5

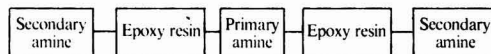
A chief advantage of cathodic E/D coatings is claimed to be their superior corrosion resistance, and this has been the main incentive for the author's work in this area. Initially, it was attempted to establish whether the cathodic deposition process, as such, would lead to improved corrosion resistance of the coatings. To this end the binder LR 38 was modified so that it could be electrodeposited anodically or cathodically depending on the pH. Such "amphoteric" behaviour was achieved by converting the (substituted succinic) anhydride rings present in LR 38 with 2-dimethylamino-ethanol into amino acid functions, i.e.:



Salt-spray data indicated that, on zinc-phosphated steel, cathodic E/D, indeed, led to considerably improved corrosion resistance. On bare steel, however, both cathodic and anodic coatings failed completely. Further, a number of different, amine-modified epoxy resin esters were prepared containing between 30 and 50 per cent w of drying fatty acids. These could all be deposited cathodically and again gave excellent salt-spray ratings on phosphated steel, but poor performance on bare steel. It was then concluded that: cathodic E/D prevents phosphate layer degradation, as is well-known⁵ from anodic E/D, and thus leads to superior corrosion resistance on pretreated steel; on bare steel the binders performed so poorly that comparison between cathodic and anodic E/D was not possible.

In the light of the recent discovery of the "high hydroxyl" principle, the poor performance of the early cationic systems on bare steel could be explained by their lack of sufficient hydroxyl groups (< 100 meq/100g) and their high fatty acid levels (30–50 per cent). To optimise corrosion resistance the trend should be towards essentially oil-free cationic binders, preferably based on epoxy resins and containing high levels of residual OH groups. It is interesting to note that all these features are realised in a number of cationic systems proposed in the recent patent literature.

The author's own work to develop cathodic systems with high bare steel corrosion resistance led to the preparation of a number of epoxy resin/amine adducts of the formal molecular composition:



Upon neutralisation (with lactic or acetic acid) these adducts became water soluble, but showed quite poor E/D behaviour, probably again owing to the absence of flow-promoting entities. The E/D behaviour was much improved by chemical incorporation of the monoepoxide, "Cardura" E 10. Unfortunately, in spite of the many hydroxyl groups present, all of these binders failed to cure sufficiently well with external crosslinkers (melamine or phenolic resins). This undoubtedly is due to the lack of catalysing acidic functions and to the retarding influence of the amino groups.

*The formulations described in Table 9 are covered by recent patent applications.

It was attempted to incorporate catalysing acidic groups into such binders and it was found that sulfanilic acid ($p\text{-NH}_2\text{-C}_6\text{H}_4\text{-SO}_3\text{H}$) co-reacts with epoxy resins in the presence of other amines, leaving the $\text{-SO}_3\text{H}$ group intact. An optimised binder of this type (Table 9) crosslinks well and leads to coatings with excellent salt-spray resistance both on phosphated and bare steel. A drawback to this binder is its rather low pH in aqueous solution (4.5–5.0), and work on cathodic systems with higher pH is, therefore, being carried out.

Table 9
Some details on composition and performance
of an "high-hydroxyl" cathodic "Epikote" E/D binder

| Binder | Development product | | |
|-------------------|---------------------|--------|-------|
| | Composition | weight | moles |
| "Epikote" 1001 | 72.1 | 3.0 | |
| Diethanolamine | 5.3 | 2.0 | |
| Ethanolamine | 1.2 | 0.75 | |
| 1,6-diaminohexane | 2.9 | 1.0 | |
| Sulfanilic acid | 1.1 | 0.25 | |
| "Cardura" E 10 | 17.4 | 2.75 | |

| Performance of an E/D applied clear film, 25 μm 30 min/180°C stoving, epoxy binder/HMMM ratio 80/20 | |
|---|---------------------------------|
| E/D behaviour | good, only pH too low (4.5–4.8) |
| Bath stability 23°C, 14 days | good |
| Crosslinkability | good |
| Salt-spray resistance | good |
| on Bonder 97 | good |
| on Steel | good |
| OH-content in film meq./100 g | 550 |

Epoxy resin emulsions for two-pack ambient temperature curing systems

In recent years a developing interest has been shown in aqueous two-pack epoxy resin emulsion coatings, either under the pressure of legislation or simply from necessity, because proper ventilation of the working areas during application of the paint could not be provided under practical conditions.

The first formulations appearing on the market were mainly intended for application to concrete, asbestos, cement and other non-metallic substrates. Later formulation work showed that by proper pigmentation, tendencies to rust spotting during application could be overcome, and this widened the scope of these coatings to include application on steel. Also of interest was the possibility of using coal tar in these formulations. Firstly, coal tar lowers the cost and secondly, it improves the water resistance of the coating.

The epoxy resin systems involved basically consist of a liquid epoxy resin of low viscosity in the usual epoxide molecular mass (EMM) range of around 200, and a liquid curing agent of the amino-amido resin type or similar. Both components are readily emulsifiable in water and the emulsions so formed are sufficiently stable for practical use.

In the formulation of paints, special care has to be taken because of the necessity of using various additives for purposes such as pigment wetting, ease of mixing of base/hardener components, flow improvement, can

stability and prevention of rust in the can. The pot-life of these systems is limited and is of the order of a few hours at ambient temperature. An important aspect here is that the end of the useful pot-life should be clearly noticeable, otherwise inferior film performance may result.

The work carried out has led to the development of a new resin, designated as "Epikote" 255. This resin has an EMM of 182–212 and a viscosity at 25° of 10–19 poise. It can be cured by a number of commercially available curing agents, although some may require dilution with water to give greater ease of mixing with the base component.

As stated above, the use of various additives in the preparation of either emulsions or paints is important and it has been frequently found that insufficient attention is paid to this, which leads, almost inevitably, to difficulties. For instance, a paint manufacturer accustomed to using sodium benzoate in his emulsion (in order to prevent rusting in the can) will be inclined to do so also when using "Epikote" 255. Severe instability of the emulsion will then be experienced.

It should thus be emphasized that inhibitors, such as sodium benzoate, are unsuitable for aqueous epoxy emulsions because, for optimum stability and reactivity with the curing agent, a fairly narrow pH range of 7.5–8.5 has to be maintained.

For in-can stability of all the starting formulations the addition of sodium metaborate, an anticorrosion pigment, is recommended. This does not have much effect on the pH, and furthermore it imparts fungicidal properties to the paints.

The dispersibility of pigmented "Epikote" 255 in water is excellent, but any large change in the pH, in either acidic or basic directions, will cause flocculation and/or phase separation. Pigments and additives must thus be selected to minimise changes in the pH of the aqueous phase. Fluctuations in the pH of the dispersion are, however, inevitable since all pigments contain water-soluble salts which slowly leach into the aqueous phase. Therefore, the effect of adding compounds which act as pH buffers was examined in "Epikote" 255 emulsions. Furthermore, these materials often improve the ease of emulsification of the resin and also act as sequestering agents (i.e. stabilising the

dispersion) by isolating the resin-wetted pigment particles from the aqueous phase.

However, some of these chemicals (often, for simplicity, referred to as sequestering agents) may react with epoxide groups and, therefore, the effect of a number of agents on the stability of aqueous "Epikote" 255 emulsions has been examined. The effects of the following components were investigated: magnesium chloride ($MgCl_2$), zinc nitrate ($Zn(NO_3)_2$), ammonium dihydrogen phosphate ($NH_4-H_2PO_4$), ammonium thiocyanate (NH_4SCN), citric acid ($C_6H_8O_7 \cdot H_2O$) and sodium hexametaphosphate ($Na(PO_3)_6$).

Aqueous emulsions of 255, at 70 per cent w solids containing the various materials, were heated for 15 minutes at 75–80°C whilst stirring. The emulsions were stored at 23°C for two months and then tested for pH, epoxide content, viscosity and emulsion stability.

The results are given in Table 10 and it can be seen that most of the sequestering agents can be used without jeopardising the emulsion stability of 255. The only material which is *not* suitable is sodium hexametaphosphate. Table 11 gives a simplified survey of the various additives used in 255 systems, along with a concise description of their function, chemical type and recommended concentration.

The aqueous "Epikote" 255 paints developed initially contained 45–55 per cent w water and were suitable for application by brush, roller or spray without further thinning. The cost of applying a multicoat system (necessary for an optimum finish), and the difficulties in removing the large volumes of water released from the films during cure, however, have retarded the acceptance of these systems in large scale industrial applications. Consequently, means of increasing the solids content of such systems, without adversely affecting their other properties, have been sought.

An examination of the effects that pigment/extender particle size and oil absorption characteristics have on both the viscosity and the rheological properties of "Epikote" 255/Casamid 360 based paints has resulted in the formulation of high-solids paints, suitable for application by single component airless spray units. This examination indicated that the effect of oil absorption on

Table 10
Stability of "Epikote" 255 emulsions at 70%w solids

| Sequestering agent ¹ | None | MgCl ₂ | Zn(NO ₃) ₂ | NH ₄ H ₂ PO ₄ | NH ₄ SCN | C ₆ H ₈ O ₇ ·H ₂ O | Na(PO ₃) ₆ |
|---|------|-------------------|-----------------------------------|--|---------------------|--|-----------------------------------|
| <i>Initial properties</i> | | | | | | | |
| Viscosity, P(23°C) | 17 | 12.5 | 21.5 | 17.5 | 8 | 14 | 13.5 |
| pH | 7.8 | 7.5 | 6.8 | 7.1 | 7.5 | 5.5 | 7.1 |
| <i>Properties after heating² and storage³</i> | | | | | | | |
| Viscosity, P(23°C) | 13.5 | 12 | 18 | 15 | 7 | 11.5 | 10 |
| pH | 7.5 | 7.5 | 6.1 | 6.8 | 7.1 | 4.6 | 6.8 |
| Syneresis ⁴ %v | 5 | <5 | 0 | <5 | 5 | <5 | 15 |
| Epoxide molar mass (EMM) ⁵ | 205 | 203 | 198 | 208 | 207 | 206 | 203 |

1. Sequester additions at 0.08 %w on the resin content.
2. At 75–80°C/15 min.
3. At 23°C/ 2 months.
4. Amount of phase separation.
5. EMM of resin used = 200.

Table 11
Additives for preparation of "Epikote" 255 emulsions/paints

| Additive | Effect | Description | Amount |
|---------------|------------------------------|--|--|
| Surfactant | Pigment-wetting | Non-ionics, such as Tween 20 Nonidet LG | 0.5 %w on pigments |
| Sequester | Buffering | Citric acid Ammonium dihydrogen-sulfate (NH ₄ H ₂ PO ₄) | 0.01–0.03 %w on pigments aiming for pH=7.3–8.3 |
| Anti-foam | Defoaming during dispersion | Non-ionic, such as AC-288 | 0.01–0.03 %w on water |
| Flow-promoter | Coalescence | Beetle 322 (a UF-type) Cerechlor (chlorinated paraffin) | 1–2 %w resin |
| Pigments | Anti-corrosion Aesthetics | Low water-soluble salt containing, neutral or slight alkaline | – |
| Curing agents | Cross-linking | Casamid-350 | 75 phr w. solid/solid |
| | | Casamid-351 | 75 " |
| | | Casamid-360 | 50 " |
| | | Versaduct-429 | 66.6 " |
| | | Anquod-100 | 50 " |

N.B. Do not add silicones—the combination of anti-foam and flow promoter already does the job properly.

application characteristics is small, but that coarser extenders with a larger particle size distribution are required to enable atomisation at high solids contents.

Table 12
High solids "Epikote" 255 paints

| Formulation | pbw | pbw |
|---------------------------------------|-------|-------|
| Base—"Epikote" 255 | 400 | 400 |
| Titanium dioxide | 320 | 320 |
| Alluvit 140 ¹ | 60 | – |
| Plastorit 0000 ² | – | 60 |
| China clay ³ | 20 | 20 |
| Entschaumer MOS ⁴ | 0.2 | 0.2 |
| 10% Citric acid solution | 0.6 | 0.6 |
| Beetle resin BT336 ⁵ | 4.0 | 4.0 |
| Tween 20 | 2.0 | 2.0 |
| Curing agent-Casamid 360 ⁶ | 400 | 400 |
| Water | 51 | 51 |
| Properties base-viscosity, poise/25°C | 72 | 65 |
| Fineness of grind, μm | 25 | 25 |
| Paint viscosity, poise. 80 %w solids | 425 | 400 |
| 75 %w solids | 246 | 180 |
| 70 %w solids | 106 | 120 |
| Gel time, hours | 2–4 h | 2–4 h |

1. Norwegian talc; Norway.
2. Plastorit Naintsch Austria.
3. ECC International, UK.
4. Borgers, Germany.
5. British Resin Products, UK.
6. Akzo Chemicals.

The paint formulations (Table 12), based on extenders with particle size distributions of 20–10 μm for Plastorit 0000 and 68 per cent < 45 μm for Alluvit 140, were successfully applied at viscosities of 400–180 poise with a total solids content of 75–80 per cent w. The pot-lives of the mixed paints were from 3–4 hours and allowed for pre-mixing and application with a single component airless spray unit with a 0.9–1.0 mm (35–40 thou) variable spray tip at 2–6 kg/cm² air pressure.

It is realised that this brief excursion through the field of aqueous coatings is a collection of experiences obtained when exploring the possibilities of specific materials based on "Veova" polymers or epoxy resins. However, it is felt that the observations made here are of a wider significance and may be of assistance to those also engaged in struggling through this field searching, hopefully, for the answers to all the problems of making "umweltfreundliche" coatings.

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Mathematical model of growth of blisters in varnish films on different substrates

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Summary

A model for blister growth in varnish films is presented for blistering caused by a difference in water activity over the film. From this model an equation has been derived containing all the parameters which are important in blister growth. The validity of the model was checked by means of experiments in which blister formation was induced by known amounts of salt on the substrate. In previous work, different varnishes were used on stainless steel, whilst in this paper the substrate was varied.

From the results, it could be concluded that the model gives an adequate description of blister growth and that in all the cases studied, water transport to the blisters was governed by osmosis. The adhesion to the substrate and the stiffness of the film cannot stop this transport. However, these parameters do have some influence on the blister growth on account of the size of the mantle surface of the blister.

Keywords

Processes and methods primarily associated with analysis, measurement and testing

diffusion
osmosis

Properties, characteristics and conditions primarily associated with materials in general

permeability

dried or cured films

blistering

Un modèle mathématique pour expliquer la croissance de cloques en films de vernis appliqués aux divers supports.

Résumé

On présente un modèle mathématique de la croissance de cloques en films de vernis dans le cas où le cloquage est provoqué par des différences de l'activité d'eau sur l'ensemble du film. A partir de ce modèle on a dérivé une équation qui renferme tous les paramètres ayant une importance à l'égard de la croissance de cloques. On a vérifié la justesse de ce modèle au moyen des expériences où la formation de cloques était provoquée par les quantités connues de sel que l'on a déposés sur le support. Dans une étude antérieure, on a appliqué de divers vernis sur les supports d'acier inoxydable, tandis qu'en cette étude on a utilisé de divers supports.

A partir des résultats, on pourrait conclure que le modèle donne une description satisfaisante de la croissance de cloques, et que dans tous les cas qui faisaient l'objet de cette étude, le transport d'eau aux cloques dépendait de l'osmose. L'adhérence du film au support et également sa rigidité ne peuvent pas empêcher ce transport. Pourtant, ces paramètres exercent une certaine influence sur la croissance de cloques en raison de la grandeur superficielle du cloque.

Mathematisches Modell des Blasenwachstums in Lackfilmen auf verschiedenen Substraten

Zusammenfassung

Für Blasenwachstum in Lackfilmen wird ein Modell für Blasenbildung als Folge eines Unterschiedes in der Wasseraktivität über dem Film vorgelegt. Aus diesem Modell wurde eine Gleichung abgeleitet, die alle für das Wachsen von Blasen wichtigen Parameter einschließt. Die Gültigkeit des Modells wurde durch Experimente geprüft, in denen Blasenbildung durch bekannte Mengen von Salz auf dem Substrat eingeleitet wurde. In früheren Arbeiten wurden verschiedene Lacke auf nichtrostendem Stahl, in dieser Arbeit dagegen auf verschiedenen Substraten benutzt.

Aus den Resultaten konnte geschlossen werden, dass das Modell eine ausreichende Beschreibung des Blasenwachstums gibt, und dass in all den untersuchten Fällen, der Wassertransport zu den Blasen durch Osmose reguliert wurde. Die Haftung zum Substrat und die Steifheit des Films kann diesen Transport nicht verhindern. Indessen haben diese Parameter einen gewissen Einfluss auf das Blasenwachstum wegen der Grösse der Manteloberfläche der Blase.

Introduction

Ref. 1

In an earlier paper¹ a model for blister growth in varnish films was presented for blistering caused by a difference

in water activity over the films applied on stainless steel as the substrate. The model was based on the hypothesis that two conditions have to be fulfilled in order that blisters can be formed:

- (a) In the boundary layer between the varnish film and the substrate, discontinuities have to be present at which the adhesion is so weak that it can be nullified by water molecules.
- (b) A driving force has to exist for the transport of water molecules through the varnish film to the areas of detachment.

If a varnish film is applied over salt spots on a substrate and this system is immersed in distilled water, blisters will grow at the places above the salt spots, because there both conditions are fulfilled. At the salt spots the film is completely detached from the substrate, and water will diffuse through the film to the salt due to the differences in the water activities. In this process, accumulation of water above the salt spots occurs and this results in deformation of the film to form a blister.

The deformation of the film generates tensions, whose resulting effect acts at the places where the film is still attached to the substrate, namely at the edges of the salt spot. At these places, the normal components of these tensions are of importance for the process of blister growth, because the film will peel-off from the substrate if these normal forces are larger than the forces of adhesion. Thus it is evident that the blister will grow as long as transport of water to the salt in the blister takes place, and the film can be deformed and detached from the substrate. This process has been described mathematically by means of an equation in which all the parameters, important for blister growth, are included.

In the paper already mentioned, the validity of this equation was checked by measuring the growth of many blisters in various varnishes on stainless steel which was contaminated with known amounts of salt. In these experiments the parameters to be studied, such as the film thickness, permeability, amount of salt, visco-elasticity and adhesion were varied, but the adhesion of the films to the substrate was in all cases rather poor because stainless steel was used as the substrate. To be sure of the general validity of the equation, it seemed necessary, therefore, to extend the experimental study by using different substrates on which the adhesion with the varnishes was markedly different. The results of this study are presented in this paper. Furthermore, to give a proper insight into the mechanism of such a type of blistering, the complete derivation of the equation used is presented.

Theoretical model

Refs. 2-6

If a varnish film is in contact with pure water on one side and with a salt solution on the other side, the resulting process of the water transport to the salt solution is, in fact, the sum of three successive steps:

- at the side where the film is in contact with pure water: the transport to the film surface and the absorption in the film,

- diffusion through the film because of the existence of a concentration gradient,
- at the side of the film in contact with the substrate and the salt solution: the desorption of water and the sorption in the salt solution.

The second process is by far the slowest and accordingly the rate controlling step of the total process. For a mathematical description of this water transport the general theory of diffusion² can be used.

General theory of diffusion

The rate of unidirectional diffusion of a component through a membrane per unit area, the flux q , is determined by the change in chemical potential $d\mu$ over the distance dx in the membrane:

$$q = -Kc \frac{d\mu}{dx} \quad (1)$$

in which,

K = proportionality factor, representing the intrinsic mobility of the component,

c = concentration of the component in the membrane.

The chemical potential can be expressed in terms of the activity, a , of the component and the chemical potential μ_0 at standard conditions:

$$\mu = \mu_0 + RT \ln a \quad (2)$$

Substituting (2) in (1) gives:

$$q = -Kc \frac{d(\mu_0 + RT \ln a)}{dx} \quad (3)$$

At constant temperature and pressure, μ_0 is constant and, therefore,

$$q = -KRTc \frac{d \ln a}{dx} \quad (4)$$

The product term KRT is known as the Fick's coefficient or the diffusion coefficient, D . Eq. (4) can thus be written in the form:

$$q = -Dc \frac{d \ln a}{dx}$$

from which:

$$q dx = -D \frac{c}{a} da \quad (5)$$

This equation for diffusion can be used to calculate the transport of water molecules through a varnish film, if the physical boundary conditions are known. In the case of blister formation, as described in the introduction, the free side of the varnish film is in contact with pure water, whilst between the varnish film and the substrate salt spots with known amounts of salt are present. Therefore, the water activities on each side of the film are

known. Because the varnishes studied are semi-permeable, no salt transport will take place³. As a result of the water transport, the salt is first dissolved and thereafter the salt solution will be continuously diluted during blister growth. Therefore, the water activity in the blister, being dependent on the salt concentration, will increase and the transport of water into the blister will slow down. For a better understanding of this unsteady state process, the transport through a varnish film under stationary conditions will first be described.

Stationary transport through a free film

If one side of a varnish film is in contact with a salt solution with a constant water activity, a_1 , and the other side is in contact with pure water with an activity, $a_2 = 1$, the flux q of water through the film is constant. Because of the stationary physical conditions on both sides of the film, the differential equation for diffusion, eq. (5), can be integrated over the thickness, L , of the film:

$$q \int_0^L dx = qL = - \int_{a_2}^{a_1} D \frac{c}{a} da = \int_{a_1}^{a_2} D \frac{c}{a} da \quad (6)$$

The diffusion coefficient of a varnish film may depend on the water concentration, c , and on the water activity, a , in the film, which are both not constant in the direction of the flow³. For the sake of convenience, a mean diffusion coefficient \bar{D} and a mean water concentration \bar{c} will be used, defined by

$$\bar{D} = \frac{qL}{\int_{a_1}^{a_2} \frac{c}{a} da} \quad (7)$$

and

$$\bar{c} = \frac{\int_{a_1}^{a_2} c da}{a_2 - a_1} \quad (8)$$

Using these mean parameters, eq. (6) can be integrated to give:

$$qL = \bar{D}\bar{c} \int_{a_1}^{a_2} \frac{da}{a} = \bar{D}\bar{c} \ln \frac{a_2}{a_1}$$

or

$$q = \frac{\bar{D}\bar{c}}{L} \ln \frac{a_2}{a_1} \quad (9)$$

For calculation of the flux, q , the water activities on each side of the film have to be known.

The water activity of a salt solution is defined by eq. (2), in which pure water has been chosen as the standard. If equilibrium exists between a solution and the vapour above this solution, the following equation holds:

$$\mu = \mu_o(G) + RT \ln p \quad (10)$$

For water, a corresponding equation can be written,

$$\mu_o = \mu_o(G) + RT \ln p_o \quad (11)$$

in which μ_o , $\mu_o(G)$ and μ are the chemical potentials respectively of water, water vapour and the salt solution.

From the eqns. (2), (10) and (11) it follows:

$$\mu - \mu_o = RT \ln a = RT \ln \frac{p}{p_o} \quad (12)$$

With eq. (12) the activity, a , of water in a salt solution is defined by

$$a = \frac{p}{p_o} \quad (13)$$

The activity of pure water is by definition equal to unity. The phenomenon of transport of water through a semipermeable membrane from pure water at one side to salt or a salt solution at the other side, is called osmosis. Often the term "osmotic pressure" is used, which is a measure for the tendency of water molecules to diffuse through a semipermeable membrane as a result of the difference in water activities on each side. The osmotic pressure is given by:

$$\Delta\pi = \frac{RT}{\bar{V}_M} \ln \frac{a_2}{a_1} \quad (14)$$

in which,

\bar{V}_M = molar volume of water in the salt solution.

By combination of eqns. (9) and (14) the stationary flux, q , can be expressed by means of the osmotic pressure:

$$q = \frac{\bar{D}\bar{c}}{L} \ln \frac{a_2}{a_1} = \frac{\bar{D}\bar{c}\bar{V}_M}{LRT} \Delta\pi \quad (15)$$

Water transport through a varnish film to salt spots on a substrate

The transport of water to a blister, induced by a salt spot on the substrate, is a non-steady process because the salt in the blister is diluted continuously. The decrease of the salt concentration involves an increase of the water activity, a_1 , which reduces the driving force continuously during the blister growth. To enable calculation of this non-steady transport, the total process can be considered as the sum of a large number of processes over very short time intervals, so that each process is approximately stationary. For each of these short processes eq. (15) may be applied, in which the boundary conditions are fixed by the water activity on either side of the film at that moment.

At atmospheric pressure, the water activity, a_1 , of a salt solution in the blister can be calculated from an equation given by Robinson and Stokes⁴:

$$\ln a_1 = - \frac{\nu m M \phi}{1000} \quad (16)$$

in which,

ν = number of particles in the salt solution originated from one molecule of electrolyte,

m = molality in mole soluted matter per kg of solvent,
 M = molecular weight of water, and
 ϕ = molal osmotic coefficient.

The values of the molal osmotic coefficient at atmospheric pressure are known⁴ for various salt solutions. The osmotic pressure can then be calculated from the eqns. (16) and (14).

In a blister an excess pressure, P_k , compared with the atmospheric pressure on the free side of the film exists, which also has influence on the water activity of the salt solution in the blister⁵. This compressive pressure, P_k , is caused by the resistance of the film against deformation. The exact equation for water transport to a salt solution in a blister can be derived as follows: The water activity, a_1 , of a salt solution in a blister with an overpressure P_k is:

$$a_{1(1+P_k)} = \frac{P_{(1+P_k)}}{P_{o(1+P_k)}} \quad (17)$$

in which,

$p_{(1+P_k)}$ = partial vapour pressure of water above the salt solution at a pressure of $1 + P_k$ atmospheres.

$p_{o(1+P_k)}$ = partial vapour pressure above pure water at a pressure of $1 + P_k$ atmospheres.

Both terms can be related to the partial pressure at 1 atmosphere⁶ because of the equilibrium between the liquid phase (L) and the gas phase (G), for which holds:

$$\mu^L = \mu^G \quad (18)$$

Equilibrium is maintained if the changes in the thermodynamical potentials of liquid and gas are equal:

$$d\mu^L = d\mu^G$$

or

$$\left(\frac{\delta\mu}{\delta T}\right)_P dT^L + \left(\frac{\delta\mu}{\delta P}\right)_T dP^L = \left(\frac{\delta\mu}{\delta T}\right)_P dT^G + \left(\frac{\delta\mu}{\delta P}\right)_T dP^G$$

or

$$-S^L dT^L + V^L dP^L = -S^G dT^G + V^G dP^G \quad (19)$$

For isothermal conditions $dT = 0$, eq. (19) can, therefore, be simplified to

$$V^L dP^L = V^G dP^G \quad (20)$$

For the salt solution at a pressure of $1 + P_k$ atmosphere, the following are true:

$V^L = \bar{V}_M$ (molar volume of water),

$P^L = 1 + P_k$ (atmospheric pressure plus the overpressure),

$V^G = \frac{RT}{p}$ (if water vapour may be considered to be an ideal gas), and

$P^G = p$ (partial pressure of water vapour above the salt solution).

Substituting these terms into eq. (20) gives:

$$\bar{V}_M d(1 + P_k) = \frac{RT}{p} dp$$

or

$$\frac{dp}{p} = \frac{\bar{V}_M}{RT} d(1 + P_k) = \frac{\bar{V}_M}{RT} dP_k \quad (21)$$

For a change of the total pressure from 1 to $1 + P_k$ atmosphere, therefore:

$$\int_{p(1)}^{p(1+P_k)} \frac{dp}{p} = \int_1^{1+P_k} \frac{\bar{V}_M}{RT} d(1 + P_k) \quad (22)$$

After integration, the following equations are obtained:

$$\ln \frac{p(1+P_k)}{p(1)} = \frac{\bar{V}_M}{RT} (1 + P_k - 1) = \frac{\bar{V}_M}{RT} P_k$$

or

$$\frac{p(1+P_k)}{p(1)} = \exp \cdot \frac{\bar{V}_M}{RT} P_k$$

or

$$p(1+P_k) = p(1) \exp \cdot \frac{\bar{V}_M}{RT} P_k \quad (23)$$

The partial pressure of saturated water vapour is constant under isothermal conditions, therefore:

$$p_{o(1+P_k)} = p_{o(1)} \quad (24)$$

Substituting the eqns. (23) and (24) in eq. (17) gives

$$a_{1(1+P_k)} = \frac{p(1) \exp \cdot \frac{\bar{V}_M}{RT} P_k}{p_{o(1)}} = a_{1(1)} \exp \cdot \frac{\bar{V}_M}{RT} P_k \quad (25)$$

With eq. (25) the water activity, a_1 , of a salt solution at a pressure of $1 + P_k$ atmospheres is related to the water activity, a_1 , at atmospheric pressure, and to the overpressure itself.

On the free side of the varnish film, where atmospheric pressure exists, the water activity is equal to unity:

$$a_{2(1)} = 1 \quad (26)$$

Integration of eq. (5) now gives the water transport:

$$\begin{aligned} q \int_0^L dx &= qL \\ &= - \int_{a_{2(1)}}^{a_{1(1+P_k)}} D \frac{c}{a} da = \int_{a_{1(1+P_k)}}^{a_{2(1)}} D \frac{c}{a} da = \bar{D}\bar{c} \int_{a_{1(1+P_k)}}^{a_{2(1)}} \frac{da}{a} \\ qL &= \bar{D}\bar{c} (\ln 1 - \ln a_{1(1+P_k)}) = -\bar{D}\bar{c} \ln a_{1(1+P_k)} \\ \therefore q &= -\frac{\bar{D}\bar{c}}{L} \ln a_{1(1+P_k)} \quad (27) \end{aligned}$$

By substitution of eq. (25) in eq. (27) one obtains:

$$q = -\frac{\bar{D}\bar{c}}{L} \left[\ln a_{1(1)} + \frac{\bar{V}_M P_k}{RT} \right] \quad (28)$$

The transport of water can also be related to the osmotic pressure. Because

$$\Delta\pi_{(1)} = -\frac{RT}{\bar{V}_M} \ln a_{1(1)}$$

it follows that

$$\ln a_{1(1)} = -\frac{\bar{V}_M \Delta\pi_{(1)}}{RT} \quad (29)$$

By substituting eq. (29) in eq. (28):

$$q = -\frac{\bar{D}\bar{c}}{L} \left[-\frac{\bar{V}_M \Delta\pi_{(1)}}{RT} + \frac{\bar{V}_M P_k}{RT} \right] = \frac{\bar{D}\bar{c}\bar{V}_M}{LRT} [\Delta\pi_{(1)} - P_k] \quad (30)$$

Combination of the eqns. (28) and (30) finally gives the mathematical description of each stationary process of water transport through the varnish to the blister:

$$q = -\frac{\bar{D}\bar{c}}{L} \left[\ln a_{1(1)} + \frac{\bar{V}_M P_k}{RT} \right] = \frac{\bar{D}\bar{c}\bar{V}_M}{LRT} [\Delta\pi_{(1)} - P_k] \quad (31)$$

The flux, q , in eq. (31) can be determined experimentally from the growth of the blister. Because of the small compressibility of water, the total weight in grams of water in the blister is approximately equal to the volume of the blister in ml. Therefore, the value of the flux, q , is equal to the increase of the blister volume, V , per unit of curved film surface, and because a blister takes approximately the shape of a segment of a sphere or an ellipsoid, so that the area through which diffusion takes place is equal to the mantle surface, MS , of this segment, the flux, q , can be written as:

$$q = \frac{1}{MS} \frac{dV}{dt} \quad (32)$$

The increase per unit of time of a growing blister can be derived from the combination of the eqns. (32) and (31):

$$\begin{aligned} \frac{dV}{dt} &= -\frac{MS\bar{D}\bar{c}}{L} \left[\ln a_{1(1)} + \frac{\bar{V}_M P_k}{RT} \right] \\ &= \frac{MS\bar{D}\bar{c}\bar{V}_M}{LRT} [\Delta\pi_{(1)} - P_k] \quad (33) \end{aligned}$$

The blister volume as a function of time as obtained by integration of eq. (33) is then:

$$\begin{aligned} V(t) &= -\int_0^t \frac{MS\bar{D}\bar{c}}{L} \left[\ln a_{1(1)} + \frac{\bar{V}_M P_k}{RT} \right] dt \\ &= \int_0^t \frac{MS\bar{D}\bar{c}\bar{V}_M}{LRT} [\Delta\pi_{(1)} - P_k] dt \quad (34) \end{aligned}$$

In this equation the influences on the blister growth are expressed both for the osmotic pressure under atmospheric conditions and for the overpressure in the blister.

Experimental

Refs. 1, 7

To test the validity of eq. (34), the values of all the parameters in this equation have to be determined. From experiments on blistering as described in this paper, the values of all these parameters can be measured or calculated, except for the overpressure, P_k , in the blisters. To obtain some estimate of the value that such a pressure can reach in a blister, model experiments have been performed in which the varnish film is detached from the substrate by means of water which is forced under controlled pressure between the film and the substrate through a small hole in the substrate. The experiments showed that an overpressure up to 5 atmospheres was sufficient to peel-off the film, whilst the calculated osmotic pressure decreased from a few hundred atmospheres at the beginning of blister growth to dozens of atmospheres after some months. It seemed, therefore, on first sight permissible to neglect P_k with respect to $\Delta\pi$. Whether this is really justifiable has to be verified, the more so because it is of essential importance to know whether the water transport into a blister can be inhibited or stopped by an overpressure. Such an investigation has been carried out by means of comparison of the water transport through free films, for which the Payne Cup test method^{1,7} was used, with the water transport to blisters in varnishes that are applied over salt spots on different substrates. For this comparison the relation $\bar{D} \times \bar{c} = f(a_1)$, that is representative for the water transport, is calculated neglecting the pressure P_k . This method of comparison was chosen because for the blisters in one varnish-substrate combination, one $\bar{D} \times \bar{c} = f(a_1)$ curve will be found, that can easily be compared with the corresponding curve for the free film. Another possibility would be to compare the blister volume calculated with the volume experimentally found, but this has to be done for each blister separately which is a tedious procedure. If the curves for the blistering films and for the corresponding free films are identical, it would be demonstrated that P_k can be neglected.

As mentioned in the introduction, various combinations of different varnishes with different substrates have been used, to study in particular the influence of adhesion and visco-elasticity on the water transport to the blisters. The results of the first series of these experiments with epoxy, chlorinated rubber, and polyurethane varnishes over salt spots of mostly magnesium acetate on stainless steel, have already been published¹. Regrettably, an error in this paper escaped the authors' attention. The word "Free" in the subscripts of the Figures 5, 6 and 7 should be omitted.

The other substrates used, PVC, aluminium, zinc and brass show analogous results to stainless steel, as follows from the $\bar{D} \times \bar{c} = f(a_1)$ curves obtained. Some arbitrarily chosen examples are presented in the Figs. 1a, b-3a, b. All other results are analogous. In these figures the curves have been drawn only for water activities less than 0.95, because at higher activities the calculations become too inaccurate. To show the scattering of the results, in each figure the data obtained from two blisters in the same varnish-substrate combination are presented.

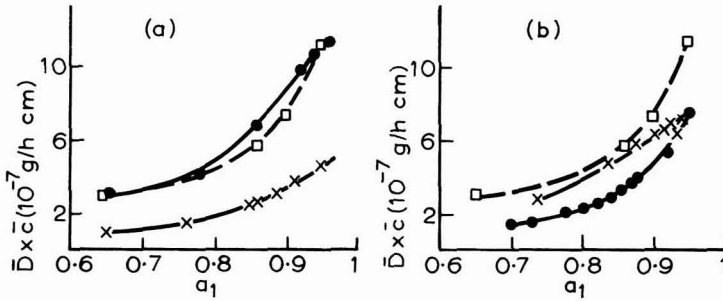


Fig. 1a. The relation of $\bar{D} \times \bar{c}$ and a_1 for polyurethane films. (●, x) blistering films on stainless steel. (□) free films

Fig. 1b. The relation of $\bar{D} \times \bar{c}$ and a_1 for polyurethane films. (●, x) blistering films on brass. (□) free films

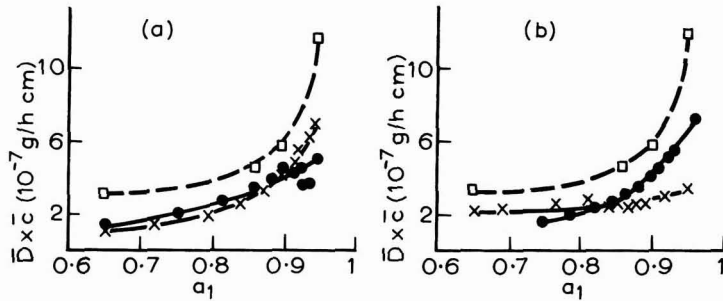


Fig. 2a. The relation of $\bar{D} \times \bar{c}$ and a_1 for epoxy films. (●, x) blistering films on stainless steel. (□) free films

Fig. 2b. The relation of $\bar{D} \times \bar{c}$ and a_1 for epoxy films. (●, x) blistering films on aluminium. (□) free films

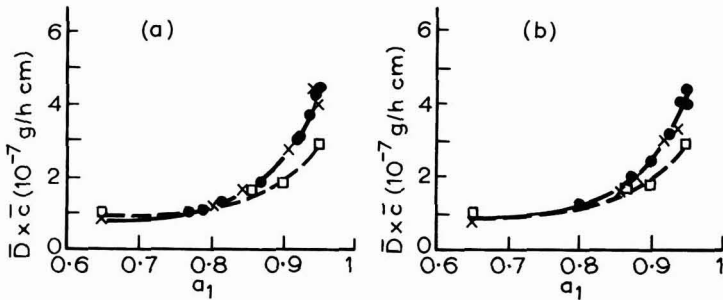


Fig. 3a. The relation of $\bar{D} \times \bar{c}$ and a_1 for chlorinated rubber films. (●, x) blistering films on stainless steel. (□) free films

Fig. 3b. The relation of $\bar{D} \times \bar{c}$ and a_1 for chlorinated rubber films. (●, x) blistering films on PVCl. (□) free films

Discussion and conclusions

Refs. 3, 8

The curves for blistering show in some cases deviations from the curves for the free film, but the maximum deviation is always of the same order of magnitude as the differences between the curves for blistering themselves.

Measuring errors due to asymmetrical detachment of the film, may have been responsible for the scattering of the results, because they introduce errors in the calculation of the parameters a_1 and $\bar{D} \times \bar{c}$. From the results it can, nevertheless, be concluded that for all varnishes on all substrates the curves for the water transport through free films show no significant differences from the curves

for water transport in blistering. It is, therefore, indeed permissible to neglect the overpressure P_k in eq. (34). Because of this, it can be concluded that the water transport to the blisters is governed by osmosis and that the adhesion and stiffness of the film cannot stop this transport.

It is worthwhile pointing out that for chlorinated rubber varnishes the blister curves agree better with the free film curve than for the other varnishes. This is caused by a more accurate determination of the base of the blisters, because the chlorinated rubber films showed blisters with a base exactly equal to the area of the salt spot. The curves for blistering in chlorinated rubber show sometimes higher values than the curve for the free film, in particular at higher water activities. An enhanced permeability by the great stretching of the film is not inconceivable. That this phenomenon did not occur with other varnishes, can be explained because the chlorinated rubber has a hydrophobic character and the other films are hydrophilic³.

Comparison of the curves for the same type of varnish on different substrates, that is for different adhesion strengths, leads to the conclusion that adhesion has no pronounced influence on the results. This supports the finding mentioned earlier that adhesion cannot stop the water transport to the blisters.

Summarising, it can be stated that the main conclusion of this study is that the growth of a blister, induced by a known amount of salt on the substrate, can adequately be described by means of eq. (34) in which the overpressure P_k can be neglected with respect to the osmotic pressure. Subsequently, it is concluded that the water transport is governed by osmosis and that the adhesion and stiffness of the film do not stop the transport. However, these parameters have some influence on the growth because the adhesion, which can vary locally, the visco-elasticity, and the film thickness determine together the shape of the blister and likewise the area of the mantle surface, MS , of the blister through which the diffusion of water takes place. The increase of the mantle surface during blister growth depends in an unpredictable way on the adhesion and visco-elasticity of the film. Therefore, equation (34), which gives a good description of the phenomenon of blister growth, has a limited predictive value. Since blistering of paint films is a very common phenomenon in practice, the model is a useful tool for a better understanding in those cases where blistering is caused by a difference in water activity over the film.

However, the following points have to be noted:

- (a) In practice the origin and the strength of the driving force for water transport are usually unknown and the water activity in the blister often does not increase as fast as in the model experiments described here. The difference in water activity over the film can remain large during blister growth in practice, for example when water soluble components are formed continuously by

hydrolysis or when a constant temperature gradient is present. In such cases large blisters can be formed.

- (b) In practice, blistering often occurs spontaneously, which means that no areas with pronounced dislocations in adhesion were present before the blisters were formed. In the cases where dislocations are absent, eq. (34) gives no relevant information because at the beginning of blistering some other mechanism must be more active than during blister growth. In such a process, the stiffness of the film and the adhesion between the film and the substrate will surely have an inhibiting influence⁸.

Acknowledgement

The authors would like to thank the staff and other employees of the Paint Research Institute TNO for their help.

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List of symbols

| | |
|-----------|---|
| a | activity of water, p/p_0 |
| c | concentration of sorbed water in a film ($\text{g}\cdot\text{cm}^{-3}$) |
| \bar{c} | mean water concentration ($\text{g}\cdot\text{cm}^{-3}$) |
| D | diffusion coefficient ($\text{cm}^2\cdot\text{h}^{-1}$) |
| \bar{D} | mean diffusion coefficient ($\text{cm}^2\cdot\text{h}^{-1}$) |
| G | gas phase |
| K | proportionality factor |
| L | liquid phase, or thickness of the film (cm) |
| M | molecular weight of water ($\text{g}\cdot\text{mole}^{-1}$) |
| MS | area of mantle surface of a blister (cm^2) |
| m | molality in mole solved substance per kg solvent ($\text{mole}\cdot\text{kg}^{-1}$) |
| P | pressure ($\text{dyne}\cdot\text{cm}^{-2}$) |
| P_k | overpressure in a blister compared with atmospheric pressure (atm) |
| p | partial water vapour pressure of a salt solution (mm Hg) |
| p_0 | partial vapour pressure of pure water (mm Hg) |
| q | flux of water through a film ($\text{g}\cdot\text{cm}^2\cdot\text{h}^{-1}$) |
| R | gas constant ($\text{cm}^3\cdot\text{atm}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$) |
| S | entropy ($\text{dyne}\cdot\text{cm}\cdot\text{K}^{-1}$) |
| T | absolute temperature (K) |

| | | | |
|-------------|--|-------------|--|
| t | time (days) | | (dyne·cm·mole ⁻¹) |
| V | volume (cm ³) | $\mu_o(G)$ | chemical potential of water vapour (dyne·cm·mole ⁻¹) |
| \bar{V}_M | molar volume of water (cm ³ ·mole ⁻¹) | v | number of particles in a salt solution, originated from one molecule of the electrolyte |
| x | distance (cm) | $\Delta\pi$ | osmotic pressure (atm) |
| μ | chemical potential (dyne·cm·mole ⁻¹) | ϕ | molal osmotic coefficient |
| μ_o | chemical potential at standard conditions | | |

Erratum

Accelerated weathering tests

By M. L. Ellinger, *JOCCA*, 1979, **62**, 136

It is regretted that on page 139 of the April issue of *JOCCA*, the units given for Langleys in the footnotes of Tables 5A and 6A were incorrect.

The footnotes should read as follows:

* The irradiation of 240,000 Langleys (1 ly = 1 g cal/cm²) is achieved within 45–60 days depending on the seasonal weather variations.

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*:

Ship's trials of oleoresinous antifouling paints. Part II: Formulations with medium and low toxicant levels by *V. Rascio, C. A. Giudice, J. C. Benítez and M. Presta*

Epoxy/polyester powder coatings—Economic and technical considerations in their usage by *J. E. Sreeves and L. Whitfield*

Emulsion paints in building by *O. C. Vorster*

Consultation before painting avoids litigation after by *E. A. Duligal*

London

Forensic Science

Following the 41st AGM on 19 April, Dr P Sansom of the Chemical Laboratory of the Metropolitan Police Forensic Science Laboratory, presented a lecture entitled, "Forensic Science", under the chairmanship of Dr T. Banfield.

Using a series of slides, some more spectacular than others, Dr Sansom enthusiastically led the audience through the steps taken to identify the cause of any incident or crime which were referred to them by the Police. The Forensic Science Laboratories took an independent view, their role being to demonstrate the guilt or innocence of suspects.

Ranging over a series of topics as wide as from the analysis of blood samples for alcohol content (over 21,000 samples were analysed last year) to the preparation of marker dyes for application to bank notes subsequently to trace thieves; from drug identification to establishing that substances as unusual as thallium had been used to poison victims; from investigation of all sorts of vehicle crashes to identifying that a particular shotgun was used to murder a cashier at a bank in Ham from glass fragments in the barrel, Dr Sansom enthralled his audience with the work of the Laboratories. Of particular interest was a description of the analytical work undertaken in identifying vehicles involved in accidents and incidents from samples of paint flakes left at the scene. The co-operation between the Laboratories, vehicle manufacturers and paint suppliers was an essential part of the success rate of the Laboratories.

In summing up, Dr Sansom stressed that, whilst the work was always varied and invariably never dull, there were certainly periods when tedious and painstaking effort was required to achieve the end result.

Following an extensive question time, a vote of thanks was proposed by Mr D. Eddowes for a most interesting and stimulating evening, to which the audience warmly agreed.

A. J.N.

Scottish

The influence of formulation on the anti-corrosive properties of paint films

On 22 March 1979, Dr G. Von Szadkowski of Bayer AG presented a lecture with the above title to a meeting of the Scottish Section held at the Albany Hotel, Glasgow.

Dr Von Szadkowski referred to his studies carried out at Bayer AG's Krefeld laboratory on the mechanism of water and water vapour transport through paint films. A simple, but nevertheless impressive method to measure this migration of water was described and it was pointed out that the transport of water, i.e. corrosion, depends largely on particle size, agglomeration and PVC.

The influence of the PVC on corrosion in simplified formulations, without extenders and additives in a long oil alkyd resin system, was shown using iron oxides as inactive pigments. Other examples made it clear how corrosion increases rapidly near the CPVC.

Having pointed out the differences between active and inactive pigments, it was explained how anti-corrosion properties of active pigments, such as zinc chromate and zinc phosphate, depend largely on the ratio of their mixture with inactive pigments.

Two new active anti-corrosion pigments from Bayer AG, AC5070 zinc ferrite and AC5071 calcium ferrite, were introduced. Judging from panels of salt spray tests, these were shown to stand up satisfactorily compared with other active pigments such as borates, molybdates, silicates, phosphates and lead-containing systems. The influence of film thickness was stated to be of major importance for comparative tests as well as the PVC and the binder systems.

Bayer AG have developed these new anti-corrosion pigments of the ferrite types to offer suitable lead and chromium free alternatives for the future.

W.L.M.

Scottish

Eastern Branch

Printing Ink Symposium for Junior Technologists

The Eastern Branch of the Scottish Section organised a one day Symposium with the above title which was held on Wednesday 17 January 1979.

It was felt by the Branch that a need arose for a Symposium of this nature which was designed principally for Junior Technologists employed in printing ink manufacture, printing and the supply and manufacture of raw materials for these processes. It was also slanted towards those already working in or representing these industries for several years.

The venue for the Symposium was Stirling University, which has excellent facilities including comfortable rooms for overnight accommodation.

The response to the Symposium was first class with 71 attending the Dinner and 170 attending the Symposium, including 38 Printing Students from the Glasgow College of Printing.

The Symposium Dinner at the Eagleton Hotel acted as an introduction for Committee Members, Lecturers and persons participating in the Symposium and it appeared that the evening was enjoyed by all.

The Symposium Chairman, Mr G. H. Hutchinson of Croda Inks, who is well known and respected within the printing ink industry, ensured the smooth running of the lectures, ably assisted by the Symposium Officers, Michael Nixon (Chairman, Eastern Branch) of Q.C. Colours Ltd, Alex McKendrick (Immediate Past Chairman) of Craig & Rose Ltd, and Tom McMahon (Publications Officer) of Croda Inks Ltd. The Lecturers represented the major printing ink manufacturers and are known for their capabilities in presenting lucid and informative lectures.

The Eastern Branch were honoured to have present the President of OCCA, Mr A. McLean and the Scottish Section Chairman, Mr I. R. McCallum, who assisted with the enquiries about the Association and its aims.

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**OIL & COLOUR
CHEMISTS' ASSOCIATION**

Newcastle Section Symposium



**ULTRAVIOLET POLYMERISATION
AND THE
SURFACE COATING
INDUSTRIES**

UV2

UV2

The eleven papers in this volume were originally published in *JOCCA* during 1978 and are based on lectures presented at the Second International Symposium of the Newcastle Section of the Association. Titles and authors are given below:

Exciplex interactions in photoinitiation of polymerisation by fluorenone amine systems by *A. Ledwith, J. A. Bosley and M. D. Purbrick*

Recent developments in photoinitiators by *G. Berner, R. Kirchmayr and G. Rist*

Present status of ultraviolet curable coatings technology in the United States by *J. Pelgrims*

The design and construction of ultraviolet lamp systems for the curing of coatings and inks by *R. E. Knight*

New developments in ultraviolet curable coatings technology by *C. B. Rybny and J. A. Vona*

Cure behaviour of photopolymer coatings by *R. Holman and H. Rubin*

Photoinitiator problems in clear coatings by *M. de Poortere, A. Ducarme, P. Dufour and Y. Merck*

The UV curing of acrylate materials with high intensity flash by *R. Phillips*

Parameters in UV curable materials which influence cure speed by *A. van Neerbos*

The use of differential scanning calorimetry in photocuring studies by *A. C. Evans, C. Armstrong and R. J. Tolman*

The UV curing behaviour of some photoinitiators and photoactivators by *M. J. Davis, J. Doherty, A. A. Godfrey, P. N. Green, J. R. A. Young and M. A. Parrish*

Copies of **UV Polymerisation**, the first volume published by the Association on this subject, are available and may be purchased separately or at the specially reduced price if purchased together with a copy of *UV2*.

The two volumes together form the authoritative work on the rapidly developing subject of ultraviolet polymerisation in the surface coatings industries. It is a work that no company in the field can afford to be without.

ORDER FORM

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Wembley, Middlesex HA0 2SF, England.

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Address to which books should be sent:

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Ultraviolet polymerisation 1 (*UV1*) £5.00 (US \$12.00) each

UV1 and *UV2* purchased together £10.00 (US \$24.00)

Prices include postage/packing (surface mail)

Lecture I. Raw materials—Present and future

J. A. L. Hawkey, FTSC, Technical Manager Information and Services, Ault and Wiborg Inks Limited:

Raw materials for printing inks should be reviewed in relation to the historical background of printing. It is emphasized that there is a continuing, inseparable relationship between ink composition with printing machinery and printing substrates.

Freedom of choice of materials depends on the printing process and end use. The differing requirements of each process are related, firstly, to the means of creating a film which can be carried to the surface to be printed. This imposes limitations on individual components associated with the effect of the material on viscosity and press stability or drying mechanism. The particular printing process defines the method of distribution and transference of a film of ink, and since the medium or varnish is fundamentally the means of transport, it is the chief variable that distinguishes liquid inks (for flexography and gravure) and paste inks (for letterpress and lithography).



A general view of the delegates attending the Printing Ink Symposium

A discussion then followed on the component materials used in liquid and paste ink varnishes and their functions contributing to printing properties, drying speed, film properties, etc. Concerning trends in pigments, a significant factor influencing selection of 'key' pigments has been the growth of four colour process printing and colour matching systems for a wide variety of print applications. Finally, in a review of raw materials and energy availability in the surface coating industries, the present heavy dependence on petroleum was underlined but with a comment on the possible exploitation and use of new alternatives from agricultural sources with continuing studies on vegetable oils, cellulose, starches and sugars.

This was a well delivered paper covering many topics that Junior Technologists would find valuable.

Lecture II. Inks for the offset litho and letterpress processes

D. E. Bissett, BSc, MIOP, Technical Liaison Executive, Coates Brothers Inks Ltd:

If the question is asked 'Can this ink be printed?', the answer will always be 'Yes', because something can

always be printed on anything. A better question is 'Can this ink be printed on a particular machine, to the required quality for a specified end-use, at an acceptable cost?'

A good formulation is, therefore, governed at one and the same time by the needs of the printing process, the interaction of the ink with the substrate involved, and the economics and end-use of the print. Sometimes the parameters involved are not very compatible, and the aim of the talk was to link together the formulation options which provide an appropriate compromise.

This was a first class lecture full of pointed questions which were well answered.

Croda Inks Limited

Film: 'Progress in printing inks'

Developments in printing inks for all the major printing processes were illustrated with reference to the principal method of ink drying, showing how advances in printing ink technology have kept pace with the requirements of the expanding printing and packaging industries. The film indicated how developments in ink-making materials, pigments, resins and film-forming polymers, had contributed to progress, leading to inks suitable for today's high speed presses and for application to an increasing variety of new papers, boards, films and metallic foils. Simple molecular models were used to help the understanding of what happens when an ink is applied to paper, and how improvements in drying and film forming properties had been achieved. In recent years, printing ink progress had been influenced by the growing attention to environmental pollution problems and in this connection, developments and applications of water-based gravure inks and ultraviolet curing inks were illustrated.

All these various aspects were illustrated by views of activities in printing ink production and quality control, and also by the actual application of products on printing presses.

Lecture III. Inks for newspaper printing

D. A. Thomas, Technical Director, Usher Walker (Inks & Rollers) Ltd:

A brief history was given of newspaper inks this century with the developments towards news inks that are in use today. Manufacturing techniques, testing procedures and packaging were also discussed. Formulations and comparisons were discussed reviewing Rotary Letterpress, Web Offset and Di-litho inks. The print and press requirements and the associated ink parameters which influence or are influenced by them were also discussed.

Developments in Di-litho and Web Offset newspaper inks were discussed, particularly coloured inks for newspapers, finally taking a look at what the future may hold for the newspaper industry.

This was a well rounded lecture covering early developments and possible future trends.

Lecture IV. Liquid inks for flexible packaging

E. P. Hickman, BSc, MIOP, ATSC, Manager Liquid Ink

Division, Mander Kidd (UK) Limited:

Flexible packaging is an area of technological growth which depends upon the development of film, foil, paper and plastic wrapping materials. The main substrates encountered in everyday use were described and the reasons for their choice in particular applications were explained.



Stirling University, the venue for the Symposium

In liquid ink formulations, the pigment is bound to the surface of a substrate with a hard resinous binder. The criteria of the selection of these components were then outlined.

Rheology of an ink was discussed, which is essential for its printability, depending upon the solution of the resin in a mixture of volatile solvents. Although there is an apparently unlimited number of solvents available from petroleum technology, the actual number which are suitable for Flexo and Gravure ink is less than twenty. However, the interactions of these solvents with each other and with the resin binders make it essential to understand the underlying physical chemistry of solvents and their mixtures.

This knowledge enables the technologist correctly to formulate a suitable solvent blend which enables an ink and lacquer to perform successfully on the printing press.

Ink manufacture was then discussed, covering mixing, blending and dispersion of pigments and resins. A résumé was given of the different types of equipment used in the ink making process.

With the exception of aqueous based inks, all liquid inks have a flammability hazard. Solvents may be harmful to health if vapours levels are not controlled.

Finally, environmental and safety considerations were discussed.

This was a totally absorbing lecture which should inspire the Junior Technologist.

Lecture V. Accelerated ink drying of printing inks

P. G. Richardson, MIOP, Technical Service Manager (Oil Inks), Fishburn Printing Co. Ltd:

A brief review was given on the conventional method of ink drying, including absorption, evaporation, oxidation/polymerisation, precipitation and combinations of these, and reasons for their current or future inadequacy where applicable, were discussed.

Present developments in lower temperature drying systems for heatset web offset were discussed with reference to the conservation of energy and to ecological considerations.

Current progress in radiation drying systems was covered, including ultraviolet, electron beam and infrared. Possible developments in the field of aqueous ink systems were discussed.

This lecture was well received, especially by the printers in the audience who are using, or planning to use, one of the radiation drying techniques mentioned above.

Lecture VI. Quality control and technical services, oil inks

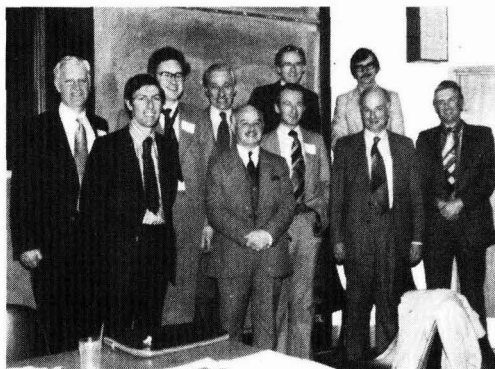
P. Gray, Lorilleux International:

Mr Gray's contribution was covered by the following headings:

- (1) Establishing print quality—Ink behaviour, (2) Different stages of technical service, (3) First aid—Ink adjustment on press, (4) Order of priorities in formulation, and (5) Quality control and some ink defects.

An excellent lecture was given concerning possibly the most important side to ink formulation and development: being fully aware of the product and how to service the product should it fail to give the desired result.

A vote of thanks was proposed by Mr I. R. McCallum (Scottish Section Chairman) to the Chairman, Lecturers and Eastern Branch Committee for a well organised Symposium.



The Symposium Committee and lecturers (left to right): Mr G. H. Hutchinson (Symposium Chairman), Mr P. Gray (Lorilleux & Bolton), Mr M. Nixon (Eastern Branch Chairman), Mr P. G. Richardson (Fishburn), Mr J. A. L. Hawkey (Ault & Wiborg), Mr D. E. Bisset (Coates Bros.), Mr A. McLean (OCCA President), Mr T. McMahon (Croda), Mr E. P. Hickman (Mander Kidd) and Mr D. Thomas (Usher Walker Ltd).

Reprints of the lectures will be given out to those attending the Symposium, but there will be copies available to Members of the Association at a cost of £3.00 for the 70 page reprint, available from Mr M. Nixon (Eastern Branch Chairman), 3E Lairds Hill, Seafar, Cumbernauld, Glasgow G67 1HH.

T.M.

Information Received

New benzene plant in production

BP Chemicals has brought into production its 250,000 tonnes a year benzene plant at Grangemouth, Scotland. The plant, which uses the BP Selective Hydrogenation process and the Lurgi Distapex process, extracts benzene from several benzene-rich feedstocks, including light gasoline from the Grangemouth gasoline treatment unit associated with the factory's ethylene cracker, and benzene concentrate from Baglan Bay factory.



The new 250 000 tonnes per year benzene plant at BP Chemicals Grangemouth factory

It consists of three main sections; the distillation section concentrates the benzene from the Grangemouth GTU to form 'B'-cut. This is then mixed with concentrate from Baglan Bay and passed to the second section where unsaturated materials are hydrogenated and sulphur compounds removed. The hydrogenated product is then passed to the Distapex section where pure benzene is produced by extractive distillation.

Change of name

At the Annual General Meeting of the George Kent Group, the shareholders approved the change of name of the parent company to Brown Boveri Kent (Holdings) Ltd; the name of George Kent Ltd will be changed to Brown Boveri Kent Ltd. The reason for the change is to emphasize the positive association of the company with Brown Boveri.

Change of address

From the beginning of July, Buhler-Miag (England) Ltd have changed their address to 19 Station Road, New Barnet, Herts EN5 1NN, England.

Epilink in UK

Akzo Chemie has commenced marketing its Epilink range of epoxy curing agents in the UK. These products have been successfully marketed in the rest of

Europe to the paint and coating industry. Amongst the range is Epilink 360, a hardener for solvent free water dispersible epoxy systems.

Change of name

Fabriek Van Chemische Producten Vondelingenplaat BV, the wholly owned Dutch subsidiary of the Penwalt Corporation of Philadelphia, who are producers of a range of industrial chemicals, have changed their name to Pennwalt Holland BV.

Colour Chemistry Department Centenary

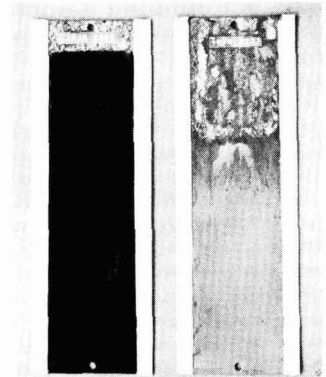
The Department of Colour Chemistry and Dyeing at Leeds University is this year celebrating its centenary. To mark the occasion, the Department organised an exhibition of the various aspects of the work being undertaken within the Department which was held in mid-May. Features on display covered the history of colour chemistry, dye application, pigments, surface coatings, printing, colour matching and the activities of the Research units.

Advanced cationic plant opened

Britain's most advanced plant for the production of cationic electropaint has been opened by Sir Barrie Heath, President of the Society of Motor Manufacturers and Traders, at the Ladywood, Birmingham factory of International Paint. The group, market leaders in industrial paint, have already spent more than £1 million on the latest equipment and advanced research for the new

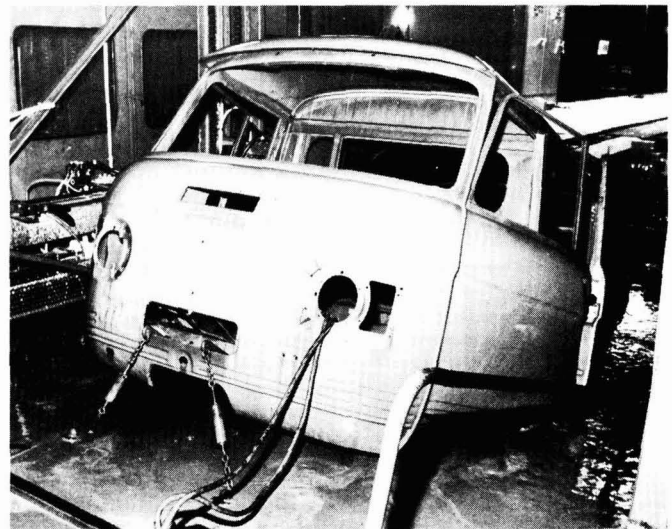
technology. A further £2 million is being invested during the next two years.

Cationic primer is acclaimed by most experts as the greatest single advance in corrosion protection in the history of the motor vehicle. It has been proven in tests that compared with the conventional anionic electropaint, cationic can give more than double the corrosion protection at the same film thickness. One



The outstanding corrosion resistance of the new cationic paint can be clearly seen in this comparison; left - cationic, right - anionic

disadvantage of the anionic system is that the important zinc phosphate pretreatment is disturbed because some dissolution of the anode, the article to be coated, occurs when resin and pigments are deposited. In addition, additives are needed to kill bacteria in most anionic tanks.



A van body emerging from the cationic electropaint tank at Chrysler UK's Dodge commercial vehicle factory at Dunstable



Sir Barrie Heath, DFC, with Mr M. Woodhouse, Group Managing Director IP, and Mr G. Snook of Massey Ferguson at the opening of the IP cationic plant

For the cationic process, the electrical circuit is reversed and the article being coated becomes the cathode. Dissolution does not occur at the cathode, and the cationic paint has a much greater resistance to bacteria and operates relatively independently of tank additives.

The advantages of cationic deposition over anionic have been known from the beginning, but anionic was developed first because there were fewer formulating problems. Cationic is a more complex material, chemically, and the biggest technical problem was to create a resin system. With the development of the resin in International ED 3002, the problems have been overcome and it is possible to produce a material of high and consistent quality.

ECC expansion

The Fordamin Co. Ltd, a company engaged in the processing and marketing of a range of industrial minerals, including marble and dolomite for the paint, rubber and plastic industries in the UK, has been acquired by ECC International (English China Clays Ltd). ECC has considerable experience in mineral processing and has a plant similar to that of Fordamin near Bristol.

Proxel biocides cleared by FDA

The Food & Drugs Administration in the USA has cleared the use of Proxel products from the ICI range of biocides in certain food-contact applications. FDA clearance, one of the most stringent in the world, means that three ICI biocides, Proxel CRL, XL2 and GXL, can be specified as preservatives in adhesives and coated papers, used in labels and packaging which come into contact with dry and fatty foods, to prevent degradation by bacterial growth. An application by ICI for their use in moist food applications is currently under consideration by the FDA.

Printing inks merger

Lorilleux & Bolton and Colora Printing Inks have announced the conclusion of negotiations resulting in an agreement for Lorilleux & Bolton to acquire the entire share capital of Colora Printing Inks Ltd in the UK, and its associate Dr Lovinsohn & Co. Ltd. The companies are active in the supply of flexographic and gravure inks and associated products. As a result of merging the resources of the companies, it is expected that they will occupy leading positions as suppliers to the expanding and technically demanding printing, packaging and converting industries.

New products

New in-line filters

Microfiltrex Ltd has announced a new range of in-line filters known as the MF4, MF5 and MF10 series, which are individually bubble point tested to ARP901 specifications, offer nominal filtration ratings extending from 2 to 20 microns and are suitable for operating pressures up to 400 bars or more, if required.

New stirrer range

Scientific and Educational Aids (ABR) Ltd, has introduced a new range of laboratory magnetic stirrers. Currently two hotplate magnetic stirrers are available and one model without a hotplate.

New Duo filter

The new space-saving Duo filter introduced by Albany Engineering Systems Europe Ltd, has been especially developed for automatic solids removal from liquids for applications with flowrates between 5 and 30 m³/hour.

A development of the successful Albany 3000 series of multiple filtration

systems, the new Duo filter incorporates the latest all welded backwash design configuration.

Densil P fungicide

Densil P, a new fungicide for paints and adhesives which combines low toxicity with a high level of effectiveness against both fungal and bacterial activity, has been launched by ICI. Major applications of Densil P fungicide in the paint industry will be the protection of dry paint films in damp environments and textured surfaces, such as masonry paints used outdoors in damp or humid climates. In the adhesives industry, Densil P fungicide will be of particular interest for the protection of wallpaper pastes.

Results of intensive tests have shown that this new ICI product, whose properties are unaffected by storage, provides long term protection against all major spoilage organisms. It has excellent weather resistance and stability to light and heat, and causes minimum discolouration. An effective bactericide, Densil P fungicide also preserves formulated products during shelf life in the can and, because it is a liquid dispersion, it is easy to use and apply.

Computer controlled spectrophotometer

Hewlett-Packard has developed a UV-visible spectrophotometer that can measure and display a 300-800 nm wide spectrum in less than a second, and besides presenting detailed spectra on an integral video display, important test data including analytical conditions and compound concentrations are shown simultaneously.

It is now possible to establish the precise quantities of as many as seven components in a single mixture, or up to a dozen components over a limited bandwidth. This advance comes from the application of reversed-optic techniques and high speed data processing.

The instrument, to be known as the HP8450A, will be available in Europe later this year and is expected to find many applications, since both substrate and the product of a reaction can be monitored simultaneously.

Paliogen Maroon L 3820

BASF has supplemented the group of perylene pigments in its Paliogen range with Paliogen Maroon L 3820, a new, highly transparent pigment which has been specially developed for automotive finishes and particularly metallics.

Conductivity controller

Pyrene Chemical Services Ltd has developed the Autobond GP conductivity controller to monitor and control the strength of a chemical solution. The Autobond GP has the advantage of a multi-electrode sensing probe, which permits control of solutions containing

solids in suspension. A build-up of solids on a single measurement sensing head can give a false conductivity reading.

Hand-held digital pH meter

Electronic Instruments Ltd has recently added a hand-held digital pH meter to its range of laboratory and field instruments. It is mains or battery operated, with a liquid crystal display ensuring good visibility.



The new model 3050 hand-held digital pH meter from Electronic Instruments Ltd

New spectrophotometers

Perkin-Elmer Ltd has introduced the model LC-75, a variable wavelength UV detector which combines excellent performance with simplicity of operation. As well as being more sensitive, having greater linearity and less drift than previous detectors, the LC-75 has an accessory auto control unit which enables the operator to carry out spectroscopic operations such as automatic stop flow scanning, automatic absorbance ratioing, wavelength optimising, auto-zeroing and baseline correction for gradient runs.

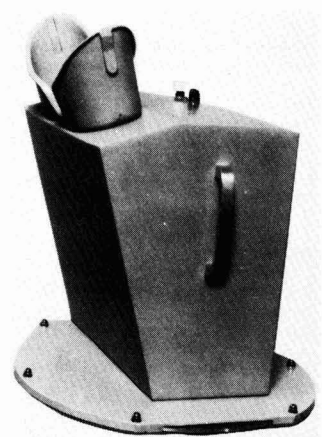
Also recently introduced is the microprocessor controlled Model 98 Series to meet growing demands placed on analytical laboratories. Covering the ranges from 4000 cm^{-1} to 200, 400 or 600 cm^{-1} , all model 98 Series instruments use an advanced version of the well established Perkin-Elmer Flowchart recording system. The flexibility required for differing applications is available in the choice of three slit programmes and six scan times.

New versatile inks

A new range of lamination inks called CTSW, suitable for use in both flexographic and gravure printing processes has been introduced by Lorilleux Bolton Clapham (Liquid Inks) Ltd. Developed to meet a strong market demand, CTSW is characterised by its ability to print on a wide range of cellulose and plastic films which are subsequently to be laminated.

Distinctness of image glossmeter

Paul N. Gardner Co. of Florida has available a new distinctness of image glossmeter which is portable, and based on the principle of matching visually the distinctness of reflected image on a sample with a comparable standard of known distinctness of image value. Six special standards are mounted on a rotating control wheel assembly, and the observer simply matches the image on the sample with a standard of known value.



The Distinctness of Image glossmeter from Paul N. Gardner Co

Conferences, courses etc.

1980 Fatipecc Congress

The fifteenth Fatipecc Congress will be held in Amsterdam, Holland from 8-13 June 1980. The theme for the Congress will be the 3E's: Ecology, energy and economy.

Colour technology courses

Instrumental Colour Systems Ltd have announced the 1979 programme of residential courses on colour technology, which will be held at Aldermaston Court near Reading. There will be three different types of course: in September there will be a general course on colour measurement and instrumentation; in November there will be an advanced course under the same heading; and in July and December there will be a total of four short courses on colour measurement for quality control.

Chemistry of carbon compounds

Elsevier Scientific Publishing Co. has published volumes IIIH and IVK of Rodd's Chemistry of Carbon Compounds, edited by S. Coffey which cover aromatic and heterocyclic compounds respectively.

Bonderite treatments brochure

Pyrene Chemical Services Ltd has available a brochure entitled "Bonderizing—the underlying strength of organic finishing", which explains the reasons for the process, methods used and the relative merits of zinc and iron phosphating.

National qualification for surface coatings

In September, the first Higher Certificate and Diploma TEC courses specifically designed for the surface coatings industry will begin. They will be run at the Polytechnic of the South Bank. Previous students in the coatings industries have had to choose between a nationally recognised HNC or HND course of limited applicability, and a highly relevant course without the status of a national award. The transfer of all higher national awards to the Technician Education Council (TEC) has allowed the design of a course which is fully relevant to the coatings industry and has the status of a nationally validated award in Physical Science.

Temperature measurement brochure

Conmark Electronics Ltd has published a new catalogue illustrating its range of digital and analogue thermometers for measuring the temperatures of gases, solids, liquids and surfaces.

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.

July

Monday 2–Tuesday 3 July

South African Division: "The role of protective coatings". Winter school to be held at the Dorothy Susskind Auditorium, University of

Witwatersrand.

September

Thursday 6 September

London Section: 1979 OCCA Golf Tournament, to be held at the Henley Golf Club, Harpsden, Henley-on-

Thames.

Thursday 13 September

Manchester Section: Technical discourse "The whys and wherefores of corrosion" to be held at UMIST, University of Manchester.



OCCA-32 Exhibition

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

NEW VENUE AND STYLE

PRELIMINARY ANNOUNCEMENT

New venue for OCCA-32

The Exhibition Committee of the Oil and Colour Chemists' Association is pleased to announce the arrangements for the 32nd Annual Exhibition which will be held from 13-15 May, 1980 at the Cunard International Hotel, Hammersmith, London W6.

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

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

Access between the two Exhibition areas will be through the intermediate Mezzanine floor, on which a small number of rooms will be available for exhibitors to display free standing exhibits.

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

The Cunard International Hotel is able to offer both exhibitors and visitors to the Exhibition a selection of restaurants, a coffee shop, bars, shopping facilities and other services available in most hotels.

Theme for the Exhibition

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

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

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

Dates and times

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

Tuesday 13 May 198009.30 to 17.30
Wednesday 14 May 198009.30 to 17.30
Thursday 15 May 198009.30 to 17.30

Travel facilities

The Cunard International Hotel is situated near Hammersmith Station on the Piccadilly Underground Line, between Heathrow Airport and the centre of London. Visitors from overseas may board the Piccadilly Line at Heathrow Central station in the Airport complex, which will take them direct to Hammersmith station or to central London where they may be staying. Car parking space at the hotel will be limited, but there is a large NCP car park close by in Kings Mall. However, those travelling to the Exhibition by car are advised to leave their vehicles outside central London and to travel to the Hotel by the Underground system.

Invitations to Exhibit

Invitations to Exhibit, giving details of the various types of exhibition facilities which will be available at OCCA-32, are now being prepared, and will be sent out shortly, together with application forms, to those companies who have exhibited at previous OCCA Exhibitions or have requested information for OCCA-32. Any organisation which has not previously shown at an OCCA Exhibition and would like to receive details should write to the Director & Secretary at the address on the Contents page.



A view of the Information Centre at the OCCA-31 Exhibition, showing the throngs of visitors to this unique annual event

International forum

At OCCA-31 in April 1979, there were direct exhibits from organisations in 15 countries, and admissions at the exhibition hall of over 8000 were recorded with visitors coming to the Exhibition from over 40 countries.

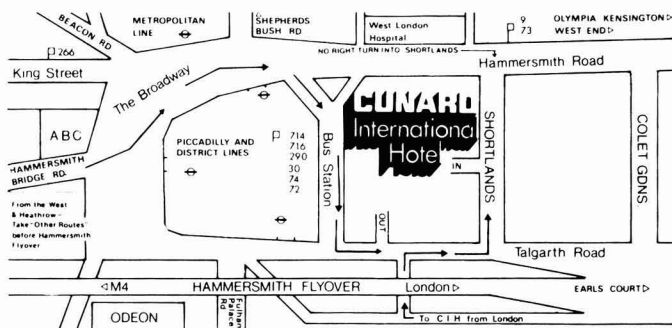
An analysis* of the tickets purchased at the entrance to the hall shows that 37 per cent of visitors came from overseas, with a significant proportion coming to the Exhibition from outside Europe.

Particularly noticeable was the high proportion of top personnel amongst the visitors, and there was a 62/38 split between technical and commercial people.

Reports coming in from exhibitors indicate that from their point of view the Exhibition was an outstanding success. For example, one exhibitor wrote in to the Association as follows:

"... our exhibit at the 31st OCCA was thoroughly successful. Frankly, we initiated substantially more business transactions than we had originally hoped for!"

*Sample of 1000 completed tickets taken from those purchased at the entrance to the Exhibition.



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

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

Official Guide

It is intended, as in previous years, to publish the *Official Guide* to the Exhibition several weeks in advance so that it

may be sent to visitors to enable them to plan the itinerary for their visits. The *Official Guide* will contain descriptions of the exhibits together with much other useful information for visitors, including maps of the exhibition areas, details of facilities, an analysis of exhibits, travel information etc. Advertising space in the *Official Guide* will be offered to those companies participating at the Exhibition, but space may also be available to other organisations. Full details of the availability of advertising space, rates, special positions etc., may be obtained from the Assistant Editor at the address on the Contents page.

London Section

1979 OCCA Golf Tournament

The London Section will be hosts for the 1979 OCCA Golf Tournament, which will be held at the Henley Golf Club, Harpsden, Henley-on-Thames on Thursday, 6 September 1979. Entrance fees for Members and their guests will be £10.50, which covers the cost of green fees, buffet lunch, evening meal, sweep and gratuities.

The number of competitors will be restricted to 60, and the presentation of prizes will take place at the evening dinner. Further details may be obtained from, and applications should be sent to, Mr B. F. Gilliam, Hon. Secretary, London Section, 25 Regency Close, Chigwell, Essex IG7 5NY (Tel: 01-534 3311 (business) and 01-501 1210 (home)).

Annual General Meeting

The 41st Annual General Meeting of London Section was held on Thursday 19 April 1979 at 6.30 p.m. at the Rubens Hotel. A total of 30 members were present at the meeting chaired by Mr D. Bayliss, Chairman.

In presenting the Annual Report, Mr B. Gilliam, Secretary, reviewed the pre-

vious year's technical programme and the attempts to create a more social atmosphere at certain meetings by having refreshments after the lecture. The attendance at evening meetings was still poor (100 different members only had attended meetings the last two years out of a total membership of 570). The request, made at the AGM, for members who do not attend to advise the Committee of the reasons for their absence, is repeated to bring to members' attention the wish of the Committee to fulfil the requirements of its members.

The Annual Report was adopted unanimously following a broad discussion on venue and technical programme composition for the coming year.

Mr D. Bannington presented the Financial Report which showed that the Section had a very small deficit, although certain receipts from the November symposium had not been received when the accounts were drawn up at year end. An exceptional expense in the year had been travel and accommodation expenses for the European Co-operation Lecturer. Discounting this item, an excess over expenditure would have been recorded. The Report was adopted without dissension.

The election of Honorary Officers of the Section was proposed from the Chair and adopted unopposed.

As only three nominations were

received for the three elected committee members, no ballot was required and Messrs J. Tooke-Kirby, E. A. Pachebat and A. C. Saxby were elected.

Dr T. A. Banfield was proposed and elected as Chairman for the 1979-80 London Section Committee.

As a final duty before handing over to Dr Banfield, Mr Bayliss thanked those Committee Members who were retiring after two years' service, Mr D. Tooke-Kirby, Mr D. Eddowes and Mr H. Lavell.

Before closing at 7.20 p.m., a small presentation of a cut glass bowl was made to Mr Bayliss, retiring Chairman, by Dr Banfield, on behalf of fellow Committee Members.

Commendation Award

Following the 41st Annual General Meeting of the London Section on Thursday 19 April 1979, the presentation of a Commendation Award, was made to Mr John Tooke-Kirby in recognition of his long and outstanding service to OCCA. In presenting the award, Mr Derek Bayliss, Immediate Past Chairman, London Section, reviewed Mr Tooke-Kirby's service and association with OCCA. Using shillings and pence as a guide to the prices of essential commodities (petrol, drink and tobacco) prevailing when Mr Tooke-Kirby first had contact with London Section, Mr Bayliss'

speech reflected the regard for Mr Tooke-Kirby held by both the London Section and OCCA.

As well as being Chairman of London Section and Southern Branch, Mr Tooke-Kirby has been on the Council for seven years, a member of the President's Advisory Committee and the Exhibition Committee.

In reply Mr Tooke-Kirby expressed his appreciation of being the recipient of the Award, hoping that there was nothing sinister in it being the 13th so to be granted by the Council.

A.J.N.

Newcastle Section

British Titan Cup

The eighteenth annual tournament for the British Titan Cup was held on Thursday, 17 May 1979 at the Blackwell Grange Golf Club, Darlington. The competition, a Stableford, was won by Mr R. Anderson of Camrex Ltd.

This is the first occasion that the competition has been held at this very



Mr R Anderson, winner of the British Titan Cup, receiving the Cup from Mr J. Clark, Chairman of the Newcastle Section.

picturesque course and also the first time it has been held in mid-week.

Twenty people took part in the com-

petition, which was played in weather conditions that may best be described as variable.

H.F.

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

ANNEVELDT, JAN JOHAN WILLEM, PO Box 12021, Jacobs 4026, South Africa. (*Natal*)

ARNOLD, FRANK VINCENT, MRIC, C Chem, Grad RIC, MSc, PhD, 3 Kiln Field, Bromley Cross, Bolton, Lancs. BL7 9HW. (*Manchester*)

COPELAND, JOHN LEONARD MUNRO, Jetmetalspray (Pty) Ltd, PO Box 43364, Industria 2042, Transvaal, South Africa. (*Transvaal*)

CUMMING, ANGUS ROBERT, PhD, BSc, ARCST, Ciba-Geigy Plastics and Additives Co., Roundthorn Estate, Wythenshawe, Manchester M23 9ND. (*Manchester*)

DALWAL, AHMED SHABAKHAN, BSc, 91 Hollyhill Road, Belvedere, Kent DA17 6HL. (*London*)

FREEMAN, LEONARD WILLIAM, Wiggins Teape Orchard Ltd, Airfield Way, Christchurch, Dorset. (*London*)

HARMAN, DENIS JOSEPH, BSc, 26 Park Road, Enfield, Middlesex EN3 6SS. (*London*)

HUGHES, GEORGE ANTHONY, Ciba-Geigy Plastics and Additives Co., 776 High Road, Tottenham, London N17 0BZ. (*London*)

LUNDBORG, BJORN, AB Sydfermiss, Box 743, 25107 Helsingborg, Sweden. (*General Overseas*)

McALLISTER, JOHN, 61 Ottoline Drive, Troon, Ayrshire. (*Scottish*)

Associate Members

BANISTER, JOHN PHILIP, Meade-King, Robinson & Co. Ltd, 501 Tower Buildings, Water Street, Liverpool L3 1BL. (*Manchester*)

EVANS, DAVID ARTHUR, 28 Brand Street, The Stewards, Benoni 1500, Transvaal, South Africa. (*Transvaal*)

HERZBERG, BERNARD, 2 The Sanctuary, Milnerton, Cape Province, South Africa. (*Cape*)

KHAN, ANJUM HAFEEZ, 29 Walter Street, Blackburn, Lancs. BB1 1RE. (*Manchester*)

STEPHENS, RICHARD LINCOLN, 57 Pound Lane, Sonning on Thames, Reading, Middlesex. (*Thames Valley*)

Registered Students

CHARLTON, BRYAN KEITH, 1 Windsor Street, Neodwana 1209, South Africa. (*Natal*)

COLEPEPER, NICHOLAS ROBERT, Lewis & Everitt (Pty) Ltd, PO Box 785, Durban 4000, South Africa. (*Natal*)

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ABOUT THE EDITOR

Dr. S. Peter Pappas, Professor of Chemistry at North Dakota State University, received his B.A. degree from Dartmouth College in 1958 and his Ph.D. degree in Chemistry from the University of Wisconsin in 1962.

Dr. Pappas has authored (or co-authored) over 30 journal articles on synthesis, reaction mechanisms, photochemistry, and coatings technology, including a recent review paper on photochemical aspects of ultraviolet curing. His papers on the photochemistry of pigments as related to chalking and uv curing, received first prize in the Roon Award Competition, sponsored by the Federation of Societies of Coatings Technology in 1974, 1975 and 1976.

ABOUT CO-AUTHORS

In preparation of "Ultraviolet Curing: Science and Technology" Dr. Pappas has been assisted by several internationally recognized authorities from major industrial firms. The editor and each co-author have contributed at least one chapter, in their respective field of specialty, to "UV Curing: Science and Technology." Co-authors and their affiliations are listed below.

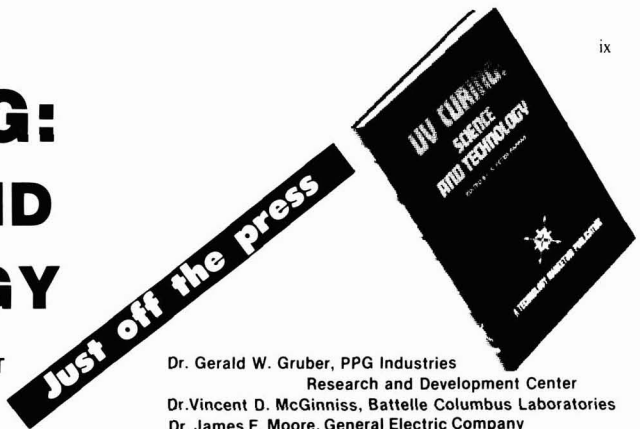
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North Dakota State University

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Topics will be introduced and discussions will be led by well known experts from industry and from the Corrosion and Protection Centre at UMIST. The aim will be to achieve maximum involvement and learning by participants.

The Discourse will be held at UMIST (University of Manchester) on 13 September 1979. Accommodation is available, in a University Hall of Residence for the night of 12 September (Tel: 061-740 1460 ext. 2562 before 1 July). Advance information is available from:

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