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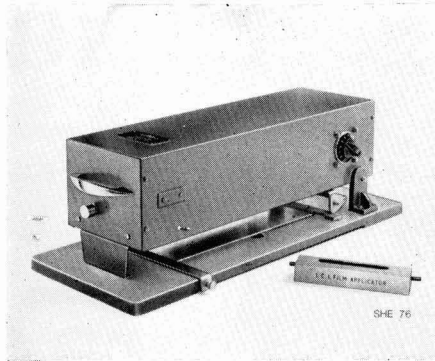Telephone 01-908 1086 Telex 922670 (OCCA WEMBLEY)
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A

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Transactions and Communications————————————

Photodegradation of polymers *

By I. C. McNeill

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Summary

The variable factors important in the photodegradation of polymers are considered and the basic processes involved in this type of degradation are outlined. The behaviour of a number of polymers which have been investigated in detail under controlled conditions is discussed and some general conclusions are drawn. The emphasis throughout is on photolysis in the absence of air, but some key references are cited covering aspects of the photo-oxidation of polymers.

Keywords

Raw materials: binders (resins, etc.)

  acrylic resin
  methacrylate resin
  styrene resin

Processes and methods primarily associated with drying or curing of coatings

  photo-oxidation
  ultraviolet curing

La photodégradation de polymères

Résumé

On considère les facteurs variables qui exercent une influence importante sur la dégradation de polymères et l'on trace les grandes lignes des processus de base qui jouent un rôle dans ce genre de dégradation. On a étudié sous des conditions verifiées et dans une manière détaillée le comportement d'une série de polymères que l'on discute et en tire certaines conclusions. Il s'agit en grande mesure de la photolyse anaérobie, mais on cite des réferences-clés sur certains aspects de la photo-oxydation de polymères.

Photodegradierung von Polymeren

Zusammenfassung

Die variablen, für die Photodegradierung von Polymeren wichtigen Faktoren werden betrachtet, und die grundsätzlichen, für diesen Degradationstyp in Frage kommenden Grundprozesse skizziert. Das Verhalten einer Anzahl von gründlich, unter kontrollierten Bedingungen untersuchten Polymeren wird besprochen und daraus werden einige Schlüsse allgemeiner Art gezogen. Die Betonung liegt durchweg auf Photoanalyse bei Abwesenheit von Luft, aber einige "Schlüsselreferenzen" werden gennant, welche Gesichtspunkte der Photooxidation von Polymeren betreffen.

Introduction

The word "photodegradation" describes two main types of degradation process initiated by light. When a reaction is carried out in the absence of oxygen, the process is described as "photolysis" and when it takes place in air or oxygen, the name "photo-oxidation" is applied. A third situation arises when degradation occurs under irradiation at an elevated temperature, but below the temperature necessary for purely thermal degradation; this type of process is referred to as "photothermal degradation".

A study of the photodegradation of polymers is more difficult than a study of thermal degradation, and comparisons of the results of different workers cannot always readily be made, because of the very large number of variable factors in these reactions. It is appropriate, therefore, to start by noting these variable factors.

With regard to the sample itself, two features are of paramount importance, the nature of any chromophores present and the glass transition temperature of the polymer. The form of the sample is also a major aspect to be considered; that is, whether it is lump, powder, film or solution. The last two forms are those preferred for detailed studies. Impurities or additives (such as sensitiser) are important, when these can absorb light energy.

The atmosphere surrounding the sample affects the mode of breakdown. Oxygen has a particular role because of its reactivity in photo-oxidation reactions, but there can sometimes be differences in behaviour between reactions carried out in, say, a vacuum and in nitrogen. This is because the escape of small volatile molecular species from the sample will be easier under vacuum. Temperature is also extremely important, and its effect is concerned with two related properties, the mobility of polymer molecules and the permeability of the sample towards either a reactive atmosphere diffusing into it, or reaction products diffusing out. Because of this, polymers may show markedly different behaviour at above and below their glass transition temperatures.

The amount of energy supplied to the sample to bring about photodegradation depends on the wavelength and intensity of the radiation used and on the degree of penetration into the sample. The term "photodegradation" generally implies the use of ultraviolet radiation, the readily available wavelengths being 254 and 365 nm. Irradiation with high energy electron beams is in some respects similar in its effects, but the input of energy and the degree of penetration into the sample are substantially greater than for ultraviolet irradiation. The complexity of the degradation process is correspondingly increased. For the purpose of this review, only those degradations induced by ultraviolet radiation will be considered.

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*Paper presented at the Newcastle Section's symposium on "Ultraviolet polymerisation" held at Durham University on 10 and 11 April 1975.

C

In experimental investigations of photodegradation, a number of features can be studied. These include (a) evolution of volatile products, (b) molecular weight changes, (c) sol/gel relationships, (d) changes in ultraviolet and infrared spectra and, where relevant, (e) oxygen uptake. Quantum yields for products and for bond scissions per molecule are obtainable in some cases.

Basic processes involved

The main processes involved in the photolytic degradation of polymers will be considered in general terms before particular systems are discussed in detail. There are three or, in some cases, four basic steps:

Absorption of the incident radiation

If the polymer is to absorb directly, it must have a strong absorption band in the region of the wavelength of light used. Otherwise, an added sensitiser (such as benzophenone) or an impurity (for example, traces of residual solvent) might absorb the light and a transfer of energy to the polymer might then occur.

Homolysis of the polymer molecule

Heterolytic bond scission to give ionic species is not encountered in this type of degradation. Homolysis to give radicals may occur preferentially at one type of bond, or more commonly, it may occur at different sites. The mode of homolysis is influenced by the energy of the incident light. Thus, because the carbon-hydrogen bond energy is significantly higher than that of either the carbon-carbon or carbon-oxygen bond, it is not susceptible to 365 nm radiation, whereas under 254 nm radiation, C-H bond scission may sometimes occur.

Chain scission

This may occur directly by rupture of one of the backbone C-C bonds or indirectly as a consequence of homolysis elsewhere in the polymer molecule. Chain scission is revealed by a fall in molecular weight of the sample.

Crosslinking

This is often observed as a sequel to homolysis. It is indicated by a rise in molecular weight and the formation of an insoluble gel.

The situation is in many cases complicated by the simultaneous occurrence of scission and crosslinking.

Photo-oxidation can involve all the above processes together with additional effects due to the presence of oxygen. The role of oxygen can vary from one system to another.

Major studies

Refs. 1–14, 25

It is perhaps useful to list some of the investigations (from a vast number of photodegradation studies) in which photo-degradation processes have been investigated in detail under very carefully controlled conditions. These include work on poly(methyl methacrylate) by Cowley and Melville[1] and by Fox, Isaacs and Stokes[2]; on poly(n-butyl methacrylate) by Grassie and MacCallum[3]; on acrylate/methacrylate copolymers by Grassie et al[4, 5]; on poly(methyl acrylate) by Fox, Isaacs, Stokes and Kagarise[6] and by Grassie and Davis[7]; on methyl, ethyl and butyl acrylate polymers by McGill and Ackerman[8, 9]; on polystyrene by Grassie and Weir[10, 11]; and on poly(α-methyl styrene) by Stokes and Fox[12].

The subject has been reviewed fairly recently by Fox[13] and by Grassie[14] in review articles and more comprehensively in a recent book by Ranby and Rabek[25].

Poly(methyl methacrylate)

Refs. 1, 15, 2

Cowley and Melville[1] have studied the photothermal degradation of this polymer (PMMA) at above the glass transition temperature T_g. The reaction closely resembles the purely thermal reaction investigated by Grassie and Melville[15] in that the molecular weight falls and monomer is produced in high yield. At 220°C, PMMA undergoes thermal degradation at the rate of about 20 per cent per hour. At 160-200°C under 254 nm irradiation, the rate is in excess of 100 per cent per hour, although the purely thermal rate in this temperature range is negligibly slow. The reaction is a chain process involving:

(i) initiation (probably at certain chain end structures) to give a polymer radical,

(ii) depropagation (220 monomer units per quantum absorbed),

(iii) termination by reaction of polymer radicals in pairs.

No products other than monomer are formed.

Fox, Isaacs and Stokes[2] have studied the photolysis of PMMA in vacuum under 254 nm irradiation at 25°C, which is well below T_g for the polymer. Under these conditions, the molecular weight falls, the number of scissions being proportional to the number of quanta absorbed. However, only traces of monomer are produced. Other volatile materials found in small amounts include methyl formate, methanol, methane, carbon monoxide, carbon dioxide and hydrogen. The maximum "zip length" for the monomer-producing depropagation reaction is only 5.

Absorption of light occurs at the ester chromophore, then homolysis can occur in three ways:

(Monomer)

$$\text{\textasciitilde CH}_2\text{--}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{·} \quad + \quad \text{H}_2\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{COOCH}_3}{|}}{\dot{\text{C}}}}\text{\textasciitilde} \quad \longrightarrow \quad \begin{array}{l}\text{Stable}\\\text{polymer}\\\text{molecules}\end{array}$$

$$\text{\textasciitilde CH}_2\text{--}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{--CH}_2\text{--}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{\textasciitilde} \quad \longrightarrow$$

$$\text{\textasciitilde CH}_2\text{--}\underset{\underset{\text{CO}}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{--CH}_2\text{--}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{\textasciitilde} \quad + \quad \text{CH}_3\text{O·} \quad \longrightarrow \quad \text{Methanol}$$

$$\text{\textasciitilde CH}_2\text{--}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{--CH}_2\text{--}\underset{\underset{}{}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{\textasciitilde} \quad + \quad \text{·COOCH}_3 \quad \longrightarrow \quad \begin{array}{l}\text{Methyl}\\\text{formate}\end{array}$$
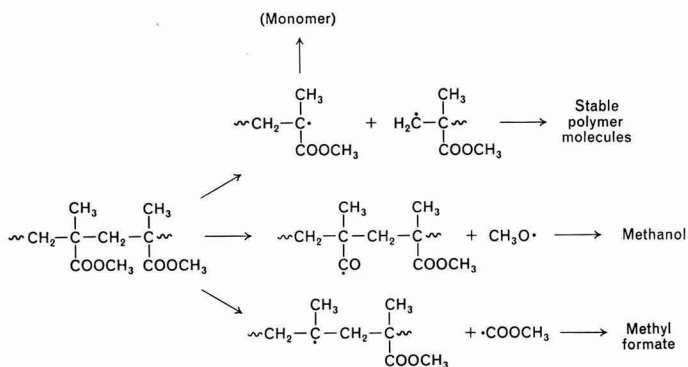
Thus the reactions above and below T_g have little in common. The difference is partly due to the fact that monomer evolution is suppressed at 25°C because of the difficulty of diffusion out of the film. The depolymerisation reaction

$$P_n \rightleftharpoons P_{n-1} + M$$

where P_n and P_{n-1} represent polymer radicals containing n and n-1 monomer units, respectively, and M represents a monomer molecule, is an equilibrium process which can proceed only from left to right if monomer is continuously removed.

The fact that the polymer itself is absorbing the incident light is confirmed by the observation that if the sample is screened by a 2mm thick sheet of perspex, radiation does not affect the sample.

Higher polymethacrylates

Refs. 3, 1

Thermal degradation of PMMA, as has been noted above, leads to chain scission and quantitative depolymerisation to monomer. Higher esters of poly(methacrylic acid) also show this reaction, but to a lesser (sometimes considerably lesser) extent. The reason for the lower yield of monomer is due to the intervention of an ester decomposition reaction leading to the formation of acid and an olefin. Thus poly(n-butyl methacrylate)[3] gives a 40 per cent yield of monomer and small amounts of butene-1. In the extreme case of poly(*tert*-butyl methacrylate)[16] the polymer breaks down to give isobutene in high yield and only traces of monomer:

$$\text{\textasciitilde CH}_2\text{--}\underset{\underset{\underset{\underset{\underset{\text{CH}_3}{|}}{\text{H}_3\text{C--C--CH}_3}}{|}}{\overset{\overset{}{\text{C=O}}}{|}}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{\textasciitilde} \quad \longrightarrow \quad \begin{array}{l}\text{Polymer}\\\text{residue}\\ +\\ \overset{\text{H}_3\text{C}}{\underset{\text{H}_3\text{C}}{>}}\text{C=CH}_2\end{array}$$
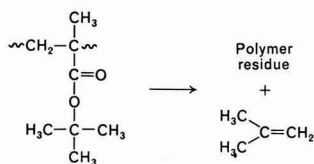
The photothermal degradation of each of these poly (butyl methacrylates) has been studied at temperatures above the T_g values, but below the temperature ($\sim$200°C) required to induce ester decomposition[3]. This leads to the interesting observation that when the reaction is photo-induced at these lower temperatures, quantitative depolymerisation occurs. The n-butyl ester polymer has been studied in some detail, and it has been found that the photothermal degradation has similar characteristics to that of PMMA, but initiation

occurs at random points along the chain and not just at the ends.

Methacrylate/acrylate copolymers

Refs. 4, 5, 24

A number of detailed studies of the photolysis of methacrylate copolymers has been carried out by Grassie and co-workers[4, 5, 24]. The comonomers included methyl acrylate, butyl acrylate, and acrylonitrile. Temperatures above T_g were employed.

For the acrylate/methacrylate systems, the presence of the acrylate units in the chains interfered considerably with the unzipping depolymerisation process characteristic of methacrylate polymers.

Poly(methyl acrylate)

Refs. 17, 6, 7

Depolymerisation is not a characteristic of polyacrylate decomposition, and this provides a marked contrast to the case of the polymethacrylates. In the purely thermal reaction above 200°C, poly(methyl acrylate), or PMA, undergoes extensive random scission to give chain fragments of various sizes. Only small yields of volatile products are reported[17].

The key to these differences in behaviour lies in the fact that the acrylate polymers have a tertiary hydrogen atom on every alternate chain carbon atom.

$$\text{\textasciitilde CH}_2\text{--}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{\textasciitilde} \qquad\qquad \text{\textasciitilde CH}_2\text{--}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}\text{\textasciitilde}$$

$$\textbf{PMMA} \qquad\qquad\qquad \textbf{PMA}$$
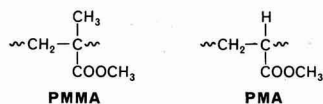
This provides a reactive site for H-abstraction processes. PMMA has no such site, and thus it is possible for depolymerisation to proceed without competition from transfer reactions.

There is also contrast in the decrease in average molecular weight (MW) the two systems. PMMA shows a slow fall in MW as degradation proceeds. This is accounted for by the fact that although many molecules disappear completely through unzipping to the chain end, some will undergo a termination before this happens, giving shorter polymer molecules, which has the effect of reducing the overall

D

average MW. The situation in PMA is much more complex: both scission and crosslinking reactions occur in the polymer; part of the degrading sample becomes insoluble, whilst the remainder shows a drop in molecular weight; and discolouration is also observed.

A careful study at room temperature of the photolysis (254 nm) of PMA films in a vacuum and in air has been carried out by Fox and co-workers[6]. The glass transition temperature of the polymer is 8°C, so that the polymer is above its T_g under the conditions of degradation. The chromophore is the same as it is in the PMMA molecule (the $-COOCH_3$ structure), so that some similarities in behaviour might be considered possible.

Fox *et al* examined (a) any changes in solubility and molecular weight, (b) the spectra of degraded films, and (c) any volatile products, which could be "trapped out" in liquid nitrogen.

In a vacuum, the number of scissions per polymer molecule increased with the number of quanta absorbed per gramme. However, crosslinking also occurred, as indicated by the formation of benzene-insoluble material. Crosslinking was less evident in air. The only spectral changes observed indicated increased carbonyl absorption for irradiation in air. Only small amounts of volatile products were formed, but the complexity of these was in contrast to the situation for thermal degradation: formaldehyde, methyl formate, methanol and carbon dioxide were estimated; carbon monoxide, methane and hydrogen (non-condensable in liquid nitrogen) were detected. Methyl acrylate was not present.

Thus there are some similarities, but also major differences in behaviour between PMA and PMMA during photolysis.

The volatile products in PMA photolysis can all be explained by homolysis within the ester group:
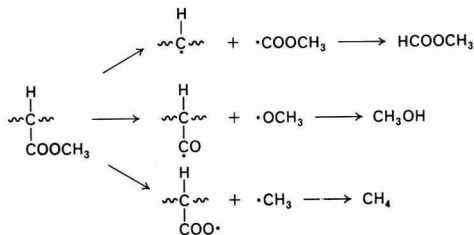
Two routes could yield formaldehyde:

$$CH_3O \cdot \rightarrow CH_2O + H \cdot$$
$$CH_3O \cdot + \cdot COOCH_3 \rightarrow CH_2O + HCOOCH_3$$
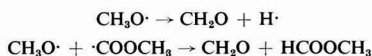
Carbon dioxide is believed to result from scission within an ester structure at the chain end following backbone scission.

Crosslinking can occur by reaction of any pair of polymer radicals. Chain scission can occur either directly in the backbone or as a sequel to the generation of the chain radicals shown above. Inter- and intramolecular transfer processes involving terminal polymer radicals are also likely to occur (as in the purely thermal degradation): these give rise to low molecular weight chains.

Thus the most distinctive differences in behaviour between PMMA and PMA are:

1. PMA crosslinks extensively; PMMA does not.

2. PMMA gives high yields of monomer above T_g; PMA gives no monomer.

These differences have proved to be characteristic of other acrylate and methacrylate polymers which have been studied.

The photolysis of PMA in solution has recently been examined in detail by Grassie and Davis[7]. The main finding of interest here is the complete absence of crosslinking when the chains are separated by solvent.

Higher polyacrylates

Refs. 8, 9

Until very recently there has been little information on the behaviour of the higher polyacrylates. This gap is now being filled by reports of work on acrylates by McGill and Ackerman[8, 9], who have compared the behaviour of the methyl, ethyl and butyl polymers under similar conditions.

The behaviour of the butyl polymer closely parallels that of PMA. The only major difference is the greatly enhanced proportion of alkane. The ethyl polymer, whilst broadly similar in behaviour, gives a greater proportion of alkane than does PMA, a much greater proportion of carbon monoxide than do either PMA or PBA, and a new type of product, acetaldehyde diethyl acetal:
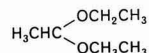
This last-mentioned product and carbon monoxide are believed to be formed in the same reaction sequence. The ethyl and butyl polymers also show the chain scission and crosslinking reactions observed for PMA.

Polystyrene and poly-α-methyl styrene

Refs. 18, 19, 10, 11, 26, 20, 12, 21

The number of polymers for which the photodegradation has been studied systematically under controlled conditions is in fact quite small. Only the styrene polymers have received the kind of attention given to the acrylates, methacrylates and vinyl ketones[18, 19].

Grassie and Weir have looked at both the photolysis[10] and the photo-oxidation[11] of polystyrene (PS) films, at 25°C. The characteristics of the vacuum photolysis are (i) gas evolution in small quantities, (ii) development of insolubility, and (iii) discolouration. There is no carbonyl-containing chromophore and although the polymer is susceptible to 254 nm radiation, it is relatively unaffected by 365 nm radiation, unless oxygen is present. The energy must be adsorbed by the aromatic ring, but there is no evidence for homolysis at the ring itself. The only volatile product proves to be hydrogen. It is not remarkable that hydrogen can be evolved well below the glass transition temperature, since it can diffuse so readily. The reaction is influenced, however, by an external pressure of nitrogen, which reduces the rate at which the hydrogen can escape from the polymer. C-H bond scission is, therefore, the homolytic reaction induced by UV light, and this seems to be centred on the weakest type of C-H bond present, namely, the tertiary H-atoms α to the aromatic ring.

$$\sim CH_2 - \overset{\overset{\displaystyle H}{\vdots}}{C} \sim$$
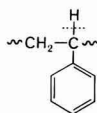
Thus the radicals generated are H· and

$$\sim CH_2 - \dot{C} \sim$$
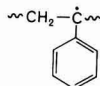
The highly reactive H· radical is likely to abstract another H-atom from the nearest available site, leading to a conjugated structure in the polymer and gaseous hydrogen:

$$\sim CH = C \sim \; + \; H_2$$
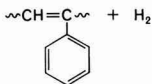
The conjugated structure accounts for the yellowing which is observed in the polymer, and which intensifies as irradiation is continued. This interpretation, however, has recently been challenged[26].

Some of the initially generated H-atoms may attack the nearest tertiary C-H structure in an adjacent molecule rather than the adjacent CH_2 in the same molecule. When this happens hydrogen is again formed, but two polymer molecules are left with adjacent radical centres. Since the polymer is well below its glass transition, these radicals are effectively in a "cage" and will probably combine forming a crosslink. This provides an explanation of the insolubilisation.

There is no similarity between the photolytic and the purely thermal degradation reactions of polystyrene. When the polymer is degraded thermally in a vacuum at above 300°C, large quantities of monomer are evolved and the molecular weight falls sharply[20]. Crosslinking, hydrogen evolution and discolouration are not observed.

Stokes and Fox[12] have studied the photolysis of poly (α-methyl styrene) or PAMS.

$$\sim CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} \sim$$

under vacuum conditions at 25° and 115°C under 253.7 nm radiation. This polymer resembles PMMA very closely with respect to the nature of its thermal degradation, when quantitative yields of monomer are produced[21].

The features of the photolytic degradation are production of small amounts of monomer (diffusion out of the film is difficult even at 115°) and a gradual reduction of the 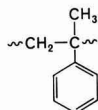molecular weight through random scission. There is also some yellowing, and small amounts of a variety of hydrocarbons are formed. One interesting feature of this reaction is that, since the monomer produced does not readily escape, it absorbs light energy and reduces the effective intensity of irradiation on the polymer.

Thus it can be seen that there is a similarity in behaviour on photolysis for PMMA with PMA and for PAMS with PS.

The two polymers with the quaternary carbon atoms give chain scission and some monomer, whereas the polymers with tertiary carbon atoms undergo crosslinking and give no monomer.

Other polymers

Many papers have appeared on aspects on the photodegradation of polyethylene and polypropylene, but the situation here is not yet clear. Fox[13] reviewed the position several years ago. In theory, these polymers should not be susceptible to degradation by UV radiation in a vacuum, since they do not contain a chromophore absorbing in this region of the spectrum. In practice, the commercial polymers are not completely regular and free from impurities. Thus some photodegradation is observed, but its study is fraught with difficulty, as is the case with any impurity effect. Both polyethylene and polypropylene show more drastic degradation under UV irradiation in air.

No fundamental study has been made of the photolysis of poly(vinyl alcohol) ($-CH_2CH(OH)-$)$_n$ but some of the features of its degradation have been reported[22, 23]. Irradiation in air leads to crosslinking and the formation of carbonyl structures. Irradiation in nitrogen in the presence of benzophenone as sensitiser results in (i) conversion of $-CHOH$ structures to carbonyl, (ii) reduction of benzophenone to benzpinacol, (iii) chain scission to give terminal carboxyl groups which lactonise, and (iv) dehydration and yellowing.

The photolysis of step-growth polymers, such as polyesters and polyamides, has not received the type of detailed study applied to some of the addition polymers. Polyesters have been reported to undergo random scission, and the polyamides both scission and crosslinking, upon irradiation in air[22,23]. Purity and film formation appear to present particular problems in investigations of these polymers. References to work on the photodegradation of several other polymers are cited by Fox[13].

Conclusions

Although comparatively few polymers have been the subject of detailed investigation, it is possible to list some of the general features which control behaviour under photolysis in the absence of air:

1. The behaviour of a particular polymer may be substantially different above and below its glass transition temperature.

2. The molecule will be directly susceptible to photolysis only if it contains a chromophore absorbing in the ultraviolet region. Carbonyl and aromatic structures have this property. In the absence of a chromophore in the polymer molecule, an impurity or an added sensitiser may absorb the light energy, and an energy transfer process may occur.

3. Polymers with the basic structure $-CH_2CXY-$, where neither X nor Y is hydrogen, undergo chain scission on photolysis.

   Depolymerisation may occur to a smaller or larger extent according to temperature. Homolysis in the side groups (for example, ester) can lead to small amounts of a variety of products.

4. Polymers with the basic structure —CH$_2$CHX— become crosslinked and insoluble. Monomer is not found, but various scission reactions can lead to small amounts of various volatile products.

Photolysis in the presence of oxygen is a much more complex process. Oxygen can in some cases limit the extent of crosslinking, if this occurs.

Since the ideal conditions for careful studies of photolytic activity exist in thin films cast from solution or solutions, it is hardly surprising that crosslinked polymeric structures are not represented in the systems investigated. Results obtained from the simpler polymeric structures would suggest that photolytically induced changes in these materials are not dramatic. Volatilisation would be extremely difficult in the network structure which pertains, and scission or cross-linking processes would simply alter the crosslink density rather than bring about fundamental changes in the character of the sample. Discolouration, however, might be feasible in certain crosslinked polymer structures.

A still more complex situation is encountered in the case of commercial photo-cured films. Not only is the polymeric structure present crosslinked, but the film will in most cases also contain residual monofunctional monomer and sensi-tiser. In addition to the basic processes of absorption, homoly-sis, chain scission and crosslinking, many degradative processes are feasible, in theory, in the photo-oxidation of such films. Most of these additional reactions, however, may well be severely restricted by the "cage" system, which prevents free movement of reactive species.

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UV-drying equipment, design and installation*

By R. E. Knight

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Summary

The types of plant suitable for the ultraviolet curing of printed matter are discussed and the factors which govern their selection are considered. The safety precautions necessary, because of the ozone produced during the process and because of the u ltraviolet radiation present, are described.

The suitability of various types of printing machine for conversion to the UV-curing process is described.

Keywords

Types and classes of coatings and allied products

  printing ink

Miscellaneous

  safety
  ultraviolet light

Processes and methods primarily associated with:

  application of coatings and allied products

  printing

  drying or curing of coatings

  ultraviolet curing

La conception et le montage du matériel pour effectuer le séchage par rayons ultra-violets

Résumé

On discute les divers types de matériel apte à effecteur le durcissement par rayons ultra-violets des imprimés et l'on considère les facteurs qui exercent une influence sur la sélection eventuelle. On décrit les précautions de sécurité exigées par l'ozone dégagé au cours du processus et en raison de la radiation ultra-violette qui se présente.

On discute l'aptitude des divers types de machines à imprimer à être adaptées au processus de durcissement par rayons ultra-violets.

Ausrüstung für UV—Trocknung—Bauart und Installierung

Zusammenfassung

Eine Besprechung der für die Ultraviolet-Härtung von Druckmaterial geeigneten Anlagen, sowie der Faktoren, welche deren Wahl bestimmen. Wegen des während der Anwendung des Verfahrens erzeugten Ozons und der dabei bestehenden ultravioletten Strahlung werden die notwendigen Sicherheitsmassnahmen beschrieben.

Besprochen wird auch die Eignung verschiedener Arten von Druckpressen, zur Umänderung für den UV-Prozess.

Introduction

There is now a variety of equipment available from various manufacturers for UV curing. Some types are fitted with flat reflectors, whilst some have elliptical or parabolic reflectors; some have only a few high-power lamps, others multiple low-power lamps. Systems can be either water cooled or air cooled, and systems employing mercury lamps, fusion lamps, impulse lamps, additive lamps and so forth, are also available. The confusion and the difficulty of selection presented to the average potential user can thus be appreciated.

The author can discuss with authority only his own company's equipment and the reasons for selecting particular features and the problems of installation. The equipment described employs the basic lamps-and-reflector configuration, which was found to give the best results in the early development work and trials carried out in America some five or six years ago. That is, the standard, medium pressure mercury arc lamp, which had already been in use for many years in the photo-printing industry and which was electrically simple in operation and of proven reliability was adopted.

The power rating of 80 watts/cm was chosen because it gave a reasonably high UV output, without dramatically reducing the lamp life—although more recent work on higher ratings (160 watts/cm) has shown that good lamp life can still be maintained with a well designed and efficient lamp cooling system. However, these higher ratings aggravate the existing and already difficult cooling problems.

The focusing elliptical reflector was adopted because at that time concentration of the UV energy was found to give the most efficient results. The author's experience and more recent research has confirmed this.

Long, high-output lamps, positioned across the print, are preferred for four reasons:

1. The configuration gives an even distribution of light across the surface, regardless of lamp life or the differential efficiency between adjacent lamps.

2. A compact arrangement is possible as the length of equipment along the sheet is not dependent upon lamp length.

3. Easy, end removal of the lamps is possible.

4. Fewer lamps are required, reducing both servicing and maintenance problems and the incidence of lamp failure.

Because of the high infrared output, shutters are necessary wherever paper, board or machinery may stop under the

lamp. Closure of these shutters is normally linked with the press or belt switch, to stop automatically.

Air for equipment and lamp cooling is used on all the systems for a number of reasons:

1. Water cooling introduces additional problems with regard to both installation and maintenance.

2. The capital cost of equipment for water cooling tends to be higher.

3. Water cooling of the reflector and shutter does not avoid the necessity to have air cooling for the lamp and in addition some form of air heat exchanger is necessary unless continuous cold water is available.

There has been confusion in the past due to a misunderstanding of the complex requirements of the cooling system. In practice these are up to five items which require cooling:

(i) The lamp body

(ii) The lamp terminals

(iii) The lamp reflector

(iv) The shutters

(v) The exposed machinery of the press or the substrate itself

and again in practice, these requirements conflict. For instance, overcooling of the lamp reduces its performance and makes it unstable; in contrast, undercooling of the shutter and reflector may cause mechanical problems.

The "water-cooled systems" generally perform only (one or more of) the cooling functions (iii) to (v) above with water, leaving the others to be done by forced air or air convection.

Safety

Ozone

A side advantage of air cooling is that the large volume of air is ample to remove the small amount of ozone produced by the lamps. Once outside the factory, ozone breaks down to oxygen very quickly and is not a lingering pollutant.

It has been found in practice that the quantity of ozone around the press is negligible and certainly lower than that produced from existing "Oxy-dry" spray equipment of the lamp type.

Corrosion by ozone has proved to be very slight and at worst produces only a fine surface defect. Normal surface finishes are adequate protection.

UV radiation

The term "radiation" is sometimes associated with radio-activity, X-rays, etc, and can, therefore, be rather misleading. It is more realistic to compare UV-curing equipment with, for example, arc welding, "sun lamps", or photo-printing—all well-known processes, which produce ultra-violet light.

Anyone who has worked in a normal engineering fabrication plant where arc welding occurs knows that personnel try to avoid "arc eye" (an eye condition caused by UV light)

mainly by looking in the other direction, even if rough screens are being used; but all welders consider at least one "dose" a necessary initiation into the trade. This last observation is not intended to belittle the risk—arc eye can be a very painful condition—but merely to put it into the correct perspective.

In Britain all installations must be approved by the local factory inspector before they can run in production. The acceptable levels of ozone and UV radiation are extremely low, but in spite of this, careful shield design and fitting by the author's company has ensured 100 per cent acceptance of equipment, up to the present time.

Several factors must be considered in shielding design:

1. Radiation per unit area decreases with the square of the distance from the lamp.

2. Radiation at such short wavelengths is absorbed by air, so the further it has to travel the weaker it becomes.

3. Reflection of ultraviolet radiation from most surfaces is poor. For example, from aluminium, 85 per cent reflection; stainless steel, 60 per cent; brass, 30 per cent; a matt black surface, less than 5 per cent.

Thus two reflections from a matt black surface, for example, will reduce the radiation to less than 1 per cent of the original value. Good shielding, therefore, involves maximising both the distance the light path has to travel and its distortion, to increase the number of reflections. Interlock switches must be fitted to all access doors.

It is important to design the equipment for maximum efficiency, in order to cope with the wide range of variables to be met in practice. These will include:

1. The variety of inks now on the market and their various drying efficiencies.

2. Variations in drying speed.

3. Variation in the thickness of print and the number of layers of colour.

4. Different printing speeds.

5. Variation in the distance from lamp to substrate.

6. Variation in the type of substrate.

The equipment must be able to cope with the worst combination of all these factors.

Installation

There are four main parts to a drying system: the lamps and reflector units; the control unit; the cooling system (fan, ducts, etc); shielding.

The choice of the number of lamps will be dictated by the printing speed, number of colours, type of substrate, etc. Broad aspects of some other factors which govern equipment design are outlined below for the three main types of printing installation (Fig. 1).
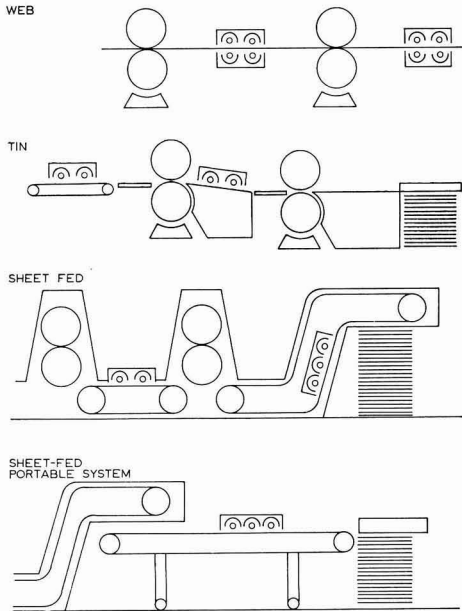
Fig. 1. Basic arrangements of UV-curing installations for various printing processes

Web

These installations are relatively simple. There is usually plenty of space available and if necessary the web can be diverted to a more convenient position. In addition, because the web can be fed through an extremely narrow gap, the shield tends can be made compact and very effective.

Metal decorating

Here there is generally a choice of two positions for the UV-drying equipment. In one case the installation is at the end between the last printing unit and the oven. There is usually a belt transfer arrangement here and fitting of the UV system across this belt is relatively simple. In the second case there are two possibilities:

Interdeck arrangement

Firstly an additional bridging system can be installed between the two presses on which the reflectors are mounted. This system is already available as an optional extra from at least one press manufacturer.

Alternatively, if the extra space is not available, it is possible to fit the units directly on to the existing sheet transfer arrangement, although in this position the equipment has to be hinged or lifted away to give reasonable access to the press.

Sheet-fed presses

These are the most difficult type of press to convert. If the lamps are to go into the press they must be inserted between the gripper bar chains before the stacker. Although the author's company has developed a very narrow reflector system for this purpose, there are still only a handful of presses to which it can be fitted without modification of the gripper spacing. Almost all the small sheet-fed units require additional press modifications.

On some of the larger presses it may be possible to gain extra space by relatively simple modification of the chain guides. A high pile extension may be available, and this too sometimes lends itself to adaptation.

However, in many presses there are only two alternatives:

1. To extend the delivery by about 1 metre—even on small presses this tends to be complicated and expensive.

2. To purchase a completely independent ultraviolet drier with belt and stacker arrangements similar to the bronzing unit. These have the advantage of being moveable from press to press, but they have several disadvantages, the main ones being: they take up a lot of space; they are a lot more expensive than a fitted system; a power point both for ventilation and power to the drying unit is necessary at each press position. Where it is possible to fit the installation on the press, the separate unit would never be recommended as an alternative.

Future prospects

Presses

It is very probable that in the future many more press manufacturers will make provisions for the installation of ultraviolet driers within the press structure, both at the end of the machine and between decks. Some are already doing this and the rest will no doubt follow at an increasingly fast rate.

Methods for modifying and fitting equipment to existing presses will be developed and become more readily available, possibly in kit form.

A wider range of free-standing, belt-type apparatus will be come available.

UV-drying equipment

Equipment will become more sophisticated as the quantity produced increases and experience is gained in its use.

More powerful lamps will become available, particularly for the short lamp application.

For multiple installations some form of heat recycling will be applied to conserve energy.

It is not considered that there will be any major innovation which will dramatically increase efficiency. The conventional ultraviolet lamps have been in use in a basically unchanged form for more than 30 years and the advent of ultraviolet-sensitive inks is not likely suddenly to transform the technology in this field. Many alternative lamp designs have been suggested, but most of these introduce additional technical problems without eliminating any of the existing ones. Some marginal increases in efficiency of cure may be obtained in this way, but only with greatly increased cost and sometimes at the expense of overall efficiency (for example, when a 50 per cent increase in power consumption is used to obtain a 10 per cent increase in efficiency of cure)—lamp efficiency should not be confused with total efficiency.

It will be difficult to find systems better than the standard mercury arc for simplicity, economy, and overall efficiency.

Ultraviolet curing inks*

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Summary

Ultraviolet-curing printing inks are already being used in the printing industry and show substantial economic advantages to the printer. The absence of solvent in these inks is also advantageous, minimising environmental pollution.

This paper attempts to outline the chemistry involved in two distinct types of photopolymerisation process, and to discuss the relative merits and disadvantages of each. Examples of photo-ionic and free radical polmerisation are given, with a brief outline of the mechanisms involved.

The types of ultraviolet light source currently in use are discussed and some mention of future developments is attempted.

Les encres d'imprimerie durcissables par rayons ultra-violets

Résumé

Les encres d'imprimerie durcissables par rayons ultra-violets sont déjà utilisées par l'industrie d'imprimerie et elles mettent en évidence un avantage économique important au point de vue de l'imprimeur. L'absence de solvant accorde un autre avantage à ces encres, la diminution de la pollution de l'environnement.

L'auteur de cet exposé essaye de tracer les grandes lignes des principes chimiques qui jouent un rôle dans les deux processus distincts de photopolymérisation, et de discuter les avantages et inconvénients de tous les deux processus. On donne, avec un bref aperçu des mécanismes intéressés, des exemples de la polymérisation photo-ionique et de celle amorcée par les radicaux libres.

On discute les divers types des sources de lumière ultra-violette qui sont utilisées actuellement et l'on fait mention de certains developpements à venir.

Durch Ultraviolet Härtende Druckfarben

Zusammenfassung

Im Druckgewerbe werden bereits durch ultraviolete Strahlung härtende Druckfarben verarbeitet. Sie bieten dem Drucker erhebliche wirtschaftliche Vorteile. Günstig ist die Abwesenheit von Lösungsmitteln in diesen Farben, wodurch Verunreinigung der Umwelt reduziert werden kann.

In dieser Abhandlung wird versucht die chemischen Vorgänge zweier unterschiedlicher Arten von Photopolymerisations-prozessen kurz zu beschreiben und von jedem seine Vor- und Nachteile zu besprechen. Es werden Beispiele von photo-ionischer und freier Radikal-Polymerisation aufgeführt zusammen mit einer kurzen Skizzierung der dabei vorkommenden Mechanismen.

Besprochen werden ebenfalls die Arten gebräuchlicher ultravioleter Lichtquellen, und es wird versucht über künftige Entwicklungen zu sprechen.

Introduction

Developments in the printing and coating industries have progressed steadily over the years. The gradual phasing out of naturally occurring resins and their replacement with synthetic polymers formulated specifically to suit the requirements of an ever demanding progressive technology has taken place. Solvents have changed, particularly in the lithographic processes; recent environmental legislation in the USA, for example, has necessitated the utilisation of petroleum distillates, having a very low aromatic content and low odour. Concomitant with this expansion in ink technology has been an improvement in the design of printing equipment and an extension in the range of printable substrates. The printing process itself has seen large changes, not only in the introduction of new technologies, but in press design, giving ever-increasing rates of output and improved quality.

Several years ago a very important development occurred in the United Kingdom—a development which many people considered would be singularly the most important techno-logical advance to occur in the history of printing inks. This was the introduction of ultraviolet-curing lithographic inks.

Conventional printing inks

Inks falling into this category are essentially those having the general composition:

       (i) resin or binder

       (ii) pigment

       (iii) solvent

       (iv) additives

The function of each of these components is well known and needs no further elaboration. The most important component to note is (iii) solvent.

There is a wide choice of suitable components, depending upon the type of printing process to be used and the nature

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of the substrate to be employed. Lithographic inks, for example, may employ one or more of the following resins: rosin esters, phenolic resins (pure and modified), maleic resins, hydrocarbon. resins. Gravure inks may utilise an even wider range, including:

Chlorinated rubber, polyamide, ethyl cellulose, cyclised rubber, resin salts (resinates), hydrocarbon resins, vinyl resins, acrylic resins, nitrocellulose.

The choice of solvent is also wide. For instance, lithographic inks utilise petroleum distillates (hydrocarbons) within a range of boiling points; gravure inks utilise alcohols, ketones, glycol ethers, toluene, water and esters; flexographic inks utilise, glycol esters, alcohols, water and esters.

This wide range of resins and solvents is necessary on account of both the type of drying or curing process to be employed and the nature of the substrate.

Ultraviolet curing systems

Any ink or coating which is to be cured by exposure to UV radiation must fulfil several requirements. These are summarised in Table 1.

Table 1

The requirements of ultraviolet-curing printing inks

1. UV-curing resins must not only polymerise readily, but must have adequate shelf stability.

2. The rate of polymerisation must be comparable with the speed of the particular process of application.

3. The final film must have acceptable adhesion to its substrate and adequate flexibility.

4. The above properties must not be adversely affected by the presence of pigment.

5. The system should be capable of wide rheological variation to cover the full range of printing processes.

6. Properties necessary for lithographic printing must be retained where applicable.

7. The system must possess low odour.

This list could be extended, but it covers the essential requirements.

The first point to arise from this list is the tremendous versatility required from a given system. At the same time, the choice of resin is more restricted because the resin system must be capable of photopolymerisation.

There is, however, some versatility within a particular system. For example, acrylic esters could be urethane acrylates, carboxylic esters formed from hydroxy acrylates, epoxy acrylates, and so on. This gives more scope in the search to obtain specific properties. There is also some versatility with regard to the type of system, and this aspect is discussed in more detail later.

Generally speaking, the ink chemist must decide the importance of each factor (speed of cure, degree of flexibility, etc) for a particular application, and choose the resin system on this basis, formulating with reference to the property most difficult to obtain.

Sources of UV light

In the UK three types of UV-curing systems are available. All employ medium-pressure mercury lamps operating at a radiative power of 80 watts per linear cm. The useful UV radiation amounts to 10-25 per cent of the emitted power, the remainder being radiation in the visible or infrared region of the spectrum.

The first type of unit utilises an elliptical reflector (Fig. 1). The UV lamp is positioned at the first focal point of the reflector, whilst the substrate passes through the second focal point. Some degree of focussing is thus achieved as light reflected internally will be focussed upon the substrate.

The IR output is a significant portion of the radiated power and the printed material must be protected from this. Protection is achieved by incorporating a shutter mechanism, which closes automatically at the instant the press stops. The lamps can also be switched to reduced power.

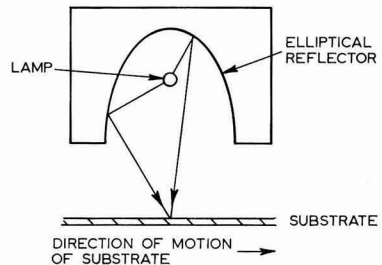Fig. 1. UV-curing system employing an elliptical reflector

There are many types of shutter design, but the most popular one in the UK involves the movement of a section of the ellipse, as shown in Fig. 2.
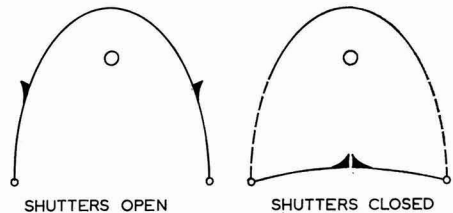

Fig. 2. A common shutter design

The second type of system employs a parabolic reflector to provide a parallel beam of light (Fig. 3).
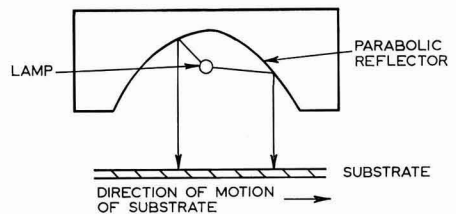

Fig. 3. UV-curing system employing a parabolic reflector

E

Both units are available with ozone-generating or ozone-free tubes, and with lamps mounted transversely across the direction of motion of the substrate.

The third type of system has lamps arranged longitudinally and employs several lamps mounted equidistant from one another at a calculated optimum height above the substrate (Fig. 4).
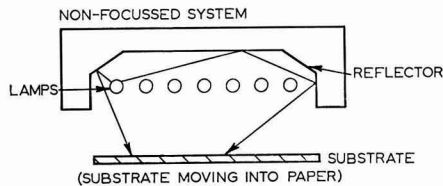

Fig. 4. UV-curing system employing lamps mounted longitudinally

The power to each lamp can be controlled individually and, depending upon the design of the print, the unit can run with varying degrees of power across the substrate. In some cases this would afford a saving in energy. There is no focusing of the radiation with this unit and the light is merely reflected from a polished aluminium surface.

In all three systems a flow of air over the lamps is required to cool the tubes, which operate at very high temperatures. The minimum air flow is governed by the flow necessary to remove adequately any ozone which may be generated. Flow rates which are high result in excessive cooling of the tubes and loss of power due to condensation of the mercury. The 80watt/cm lamp has been evolved essentially from considerations of optimum curing power, energy consumption, lamp temperature and lamp life.

## Current systems utilising photopolymerisation

Refs. 1–3

The use of acrylic esters

Acrylic esters have found considerable use in the field of photopolymerisation. They are capable of rapid polymerisation and fulfil many of the requirements outlined earlier. Several types of acrylic ester resin have been examined. Typical resins[1] are derived from the following:

Epoxy esters

(i) Bisphenol A—epichlorohydrin resins
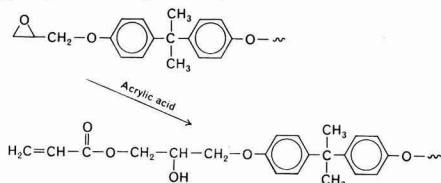
Isocyanate adducts
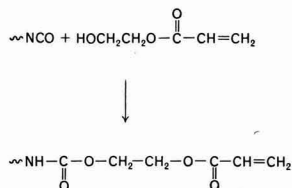
Epoxy oil acrylates
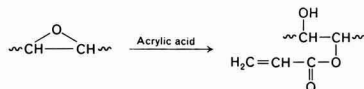
(For example, epoxidised soya oil contains 3-4 oxirane groups per molecule.)

Acrylic monomers

Monofunctional: for example, ethyl hexyl acrylate (EHA).

Polyfunctional: for example, trimethyl propane triacrylate (TMPTA) and pentaerythritol tetra-acrylate (PETA).

Methacrylic acid esters cure considerably more slowly than acrylic esters and hence have a limited use in UV-curing inks and coatings. As a general rule, however, the glass transition temperature T_g is higher for methacrylic esters, so that polymeric acrylate films based on these esters tend to be more flexible.

Combinations

Monoacrylates: good viscosity reducers.

Polyacrylates: improve cure rate.

Oligomers: provide adhesion and toughness.

Photoinitiators employed in acrylic ester systems

Benzoin ethers
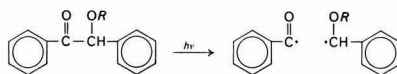
The effect of increasing the alkyl chain length (R) has little influence on the rate of cure, but does give somewhat better solubility in the UV systems.
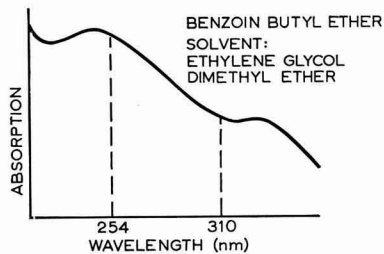
Medium-pressure mercury vapour lamps have three distinct emission lines relevant to the absorption spectrum of benzoin ethers. These are at 366, 310 and 254nm. The energy of both the 310 and the 254nm bands will give rise to free radicals. As the extinction coefficients of benzoin ethers at these two energies are very different, it would be predicted that at equal radiation intensities, the degree of penetration would be greater for the 310nm incident radiation:
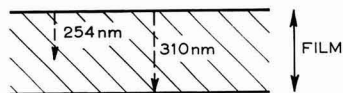
In relation to the benzoin ether absorption spectrum, low pressure germicidal lamps have a single major emission at 254nm, and these lamps would be expected, therefore, to be of little use for thick coatings.

Benzophenone
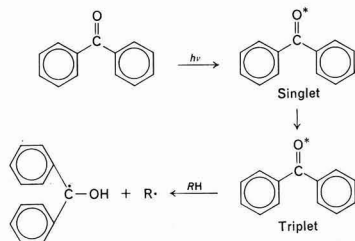
The use of benzophenone as a photoinitiator has been well studied and the mechanism documented[2]. Hydrogen abstraction (rather than cleavage) is the proposed mechanism.

The extinction coefficient E_{254} is larger for benzophenone than for benzoin ethers, and is a factor to be considered with regard to overcoming oxygen inhibition. (This will be discussed in more depth later.)

The nature of the hydrogen donor has received some attention, and a summary of the results is given in Table 2.

Table 2
The nature of the hydrogen donor in benzophenone–activated photopolymerisations

1. Active hydrogen atoms*

   (a) Alcohols $R-CH_2-OH$

   (b) Alkyl ethers $R-CH_2-O-CH_2-R$

   (c) Tertiary amines $R-CH_2-N\begin{smallmatrix}R_1\\R_2\end{smallmatrix}$

   (d) Epoxide derivatives $-O-CH_2-CH-CH_2-O-$ with OH

   (e) Polyethers $-O-CH_2-CH_2-O-CH_2-CH_2-O-$
   *The active H-atoms are given in bold type

2. Inactive hydrogen atoms

   (a) Polyesters $R-CH_2-O-\overset{O}{\overset{\|}{C}}-R_1$

   (b) Alcohols $R-CH_2-OH$

A recent review[3] has summarised the mechanisms of many of the photoinitiators currently used in acrylic esters systems.

Oxygen inhibition

Ref. 4

The scavenging effect of oxygen upon free radicals is well documented. An example is the photopolymerisation of styrene:
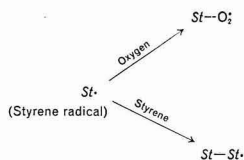
The rate of reaction of the oxygen step is greater than the rate of polymerisation by a factor of 10^6. At low concentrations of oxygen, the rate of photo-polymerisation of styrene is greater than it is in the absence of oxygen. Some $-O-O-$ linkages have been postulated for polystyrene, since it readily undergoes both thermal and radiative decomposition[4].

In addition to the above consideration, oxygen is an effective absorber of UV radiation and hence the necessity to use high powered sources of radiation.

As oxygen inhibition and UV-energy absorption play such significant roles. The distance from lamp to substrate is a very important factor in the design of UV-curing units for commercial printing presses.

These two factors can be largely overcome by:

(a) minimising the distance from lamp to substrate,

(b) introducing an inert atmosphere over the substrate,

(c) using high energy sources of UV radiation,

(d) the correct choice of photoinitiator

(and/or combinations of these four).

Photoinitiated ionic polymerisation

This technology utilises the formation of Lewis acids upon photolysis.

Schiemann reaction
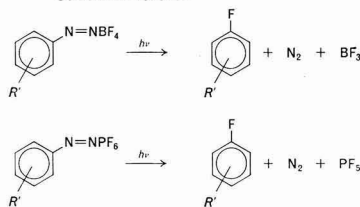
No oxygen inhibition occurs in this reaction and polymerisation proceeds readily:

(No oxygen inhibition)
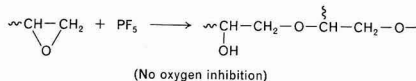
The proposed mechanism is as follows:
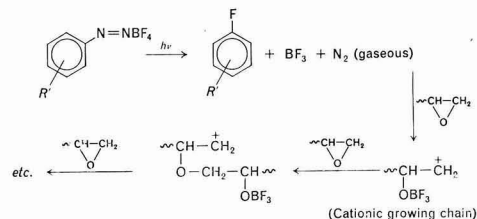
The reaction continues after the coating leaves the UV exposure zone, and polymerisation can be enhanced by following up the UV exposure with irradiation from an IR lamp.

The diazonium-salt photoinitiator can vary in concentration in the ink from 0.5 to 2.0 per cent. The depth of cure at these photoinitiator levels is adequate and transparent polymers up to 50cm thick have been reported. A low-pressure mercury arc is apparently sufficient to give practical cure times.

Disadvantages

Can stability is poor. This can be partially overcome by refrigeration (but this is obviously not economic), or by the addition of stabiliser. Several types of stabiliser are in use, but Lewis bases, such as acetonitrile, have been tried; other stabilisers have included ureas, sulfoxides and amides.

Thick films can give problems due to liberation of nitrogen. (Bubble effects in the polymerised material might be detrimental.)

The liberation of Lewis acids might cause corrosion problems.

Many diazonium salts are highly coloured and this can limit their range of application.

Advantages

The main advantage over acrylic ester photopolymers lies in the degree of shrinkage. Shrinkage during photopolymerisation could be an important factor in the adhesion of the photopolymers to their substrate. In fluid systems, shrinkage is compensated for by flow, but as viscosity increases, so adhesion problems result. If the photopolymer has a sufficiently low glass transition temperature, a "post-bake" may restore adhesion. The level of shrinkage of polymer systems is illustrated in Table 3.

In certain ring opening polymerisations, expansion can occur, for example:

Spiro-orthocarbonates
$150°C \downarrow BF_3$
$\sim 2\%$ expansion

Commercial realisation

Ultraviolet-curing printing inks have been available for several years. The technology is extensively employed in lithographic printing for numerous reasons. The advantages of UV have been adequately covered at recent symposia and in the literature.

Not only has the use of UV-curing inks brought about a realisation of the advantages ancitipated from their inception, but the quality of print and the low odour associated with these inks has given rise to demands by customers' adoption of the UV-curing system in specific areas, such as food packaging, where the low odour associated with UV-cured products gives them an advantage over oleoresinous systems.

Future developments

Resin manufacturers are now producing photopolymerisable resins and monomers tailor-made for the printing industry. Lamp suppliers are also looking to the future, and new types of lamp are emerging. Fusion lamps, pulsed lamps and additive lamps, all designed to increase the efficiency of the process, are expected to develop.

The use of electron-beam curing could well be another line of development. The problem of secondary X-ray emission has now been overcome and several laboratories are examining the potential of electron-beam initiated polymerisation.

[*Received 7 July 1975*

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2. Hutchison, J., Lambert, M. C., and Ledwith, A., *Polymer Journal*, 1973, **14**, 250.
3. Kinstle, J. F., *J. Radiation Curing*, 1974, **1** (2), 2.
4. Kodaira, *et al.*, *Polymer Journal*, 1973, **4**, 1.

Table 3

Various polymerisation processes and the differences in volume between reactants and products

Polyester formation $R_1-\overset{O}{\overset{\|}{C}}-OH + R_2OH \longrightarrow R_1-\overset{O}{\overset{\|}{C}}-OR_2 + H_2O$ (25% shrinkage)

Polyolefine formation $H_2C=\overset{R}{\underset{|}{CH}} + H_2C=\overset{R}{\underset{|}{CH}} \longrightarrow -CH_2-\overset{R}{\underset{|}{CH}}-CH_2-\overset{R}{\underset{|}{CH}}-$ (10% shrinkage)

Polyether formation $R_1-O^- + CH_2\overset{}{\underset{O}{\frown}}CH-R_2 \longrightarrow R-O-CH_2-\overset{O^-}{\underset{|}{CH}}-R_2$ (3-5% shrinkage)
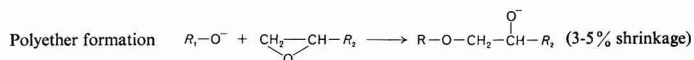
Some aspects of the pigmentation of UV-curable systems*

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Summary

The general principles involved in the curing of films by ultraviolet radiation are described and the effect of pigmentation with titanium dioxide is considered. It is found that although titanium dioxide has a high absorption value for ultraviolet radiation, when the correct combination of photoinitiators is used there is sufficient penetration to allow satisfactory cure to occur. It is also found that UV radiation is attenuated to a greater extent by a rutile pigment with a small crystal size than by one with a large crystal size, although it is not certain whether this effect is sufficiently great to have practical significance. The implications of this effect are outlined and the rheology and surface wrinkling of pigmented UV-curable paints and inks is discussed.

Keywords

Raw materials:
  prime pigments and dyes

    titanium dioxide

miscellaneous paint additives

    ultraviolet absorber

Processes and methods primarily associated with drying or curing of coatings

    photoinitiation
    ultraviolet curing

Properties, characteristics and conditions primarily associated with:

    raw materials for coatings and allied products

        particle size

    dried or cured films

        rivelling

Certains aspects de la pigmentation des systèmes de revêtements durcissables par rayons ultra-violets

Résumé

On décrit les principes généraux du durcissement des feuils par radiation ultra-violette, et l'on considère l'effet du dioxyde de titane en tant que pigment. Bien que le dioxyde de titane possède un valeur d'absorption élevé de radiation ultra-violette, on trouve qu'il y a une pénétration suffisante pour assurer un durcissement satisfaisant, pourvu que l'on utilise la combinaison convenable de photoinitiateurs. On trouve d'ailleurs que l'action atténuante du pigment de type rutile de faible grandeur particulaire est plus marquée que dans le cas où la grandeur particulaire est plus importante. On trace les grandes lignes des implications de cet effet et l'on discute la rhéologie et le frisage superficiel des peintures et des encres d'imprimerie durcissable par rayons ultra-violets.

Einige die Pigmentierung UV-härtbarer Systeme betreffende Gesichtspunkte

Zusammenfassung

Eine Beschreibung der allgemeinen, bei der Härtung von Filmen durch ultraviolette Bestrahlung in Frage kommenden Prinzipien, und Betrachtung der Auswirkung einer Pigmentierung mit Titandioxid. Es wurde festgestellt, dass, obwohl Titandioxid einen hohen Absorptionswert für ultraviolette Strahlen besitzt, sofern die richtige Kombination von Photoinitiatoren benutzt wurde, ihre Eindringung genügt, um eine zufriedenstellende Härtung zu ermöglichen. Ausserdem wurde gefunden, dass UV Strahlung viel mehr bei Anwesenheit von Rutilpigment mit geringer Kristallgrösse verringert wird, als von solchem mit grossen Kristallen, obwohl es noch nicht feststeht, ob diese Wirkung gross genug ist, um von praktischer Bedeutung zu sein. Die Implikation dieser Wirkung wird kurz dargestellt, und die Rheologie und Oberflächenschrumpfung pigmentierter UV-härtender Lack- und Druckfarben wird besprochen.

Introduction

UV-curing is essentially the use of ultraviolet radiation to convert a monomeric or oligomeric unsaturated substance into a polymer, which has the necessary adhesion to the substrate on to which it is applied, and which also possesses an acceptable level of hardness and flexibility.

The questions may be posed: Why ultraviolet radiation? What is so special about UV radiation in the initiation of polymerisation? Reference to Fig. 1 shows the position of ultraviolet radiation relative to visible and infrared radiation in the electro-magnetic spectrum. The first point to note is that the energy associated with UV radiation is higher than that of infrared or visible radiation. When a thermal cure is used in the preparation of a surface coating, it is to a large extent the energy of infrared radiation which is being used.

A molecule will heat up when subjected to infrared radiation because this region of the spectrum contains certain fre-
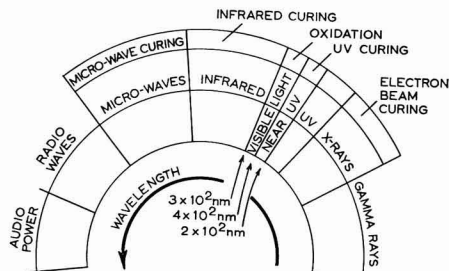

Fig. 1. The electromagnetic spectrum

quencies, which correspond to the frequencies of various modes of vibration, rotation and translation in an organic molecule.

Thermal reactions usually involve the ground electronic states of vibrational, rotational and translational energies in the upper range of their Maxwell-Boltzman distributions (Fig. 1a). In other words the reactive state is reached in a series of discrete jumps. Reactions can occur through the involvement of any one or more of these modes, as long as the energy supplied to the molecule is in excess of the minimum energy necessary for the reaction to proceed. Such a process has certain disadvantages, the major one being concerned with the many deactivation pathways along which the excited molecule may react; this may result in the formation of a wide range of products. The other major disadvantage is that the process is subject to gross inefficiency due to heat losses to the surrounding atmosphere and to the substrate. In contrast, the energy associated with UV is greater than that of either visible or infrared radiation and excited states are formed directly when photoinitiators are irradiated with UV, without excitation of intermediate vibrational, rotational and translational levels. UV radiation may be regarded as a "cold radiation", which will cause the promotion of electrons to highly reactive and long-lived excited states, making them capable of forming radicals directly or indirectly. Summarising; the advantage of ultra-violet curing arises from the fact that much of the radiation is specifically absorbed by a photoinitiator. The surrounding matrix (oligomer and monomer) is transparent or partially transparent to this exciting radiation and consequently a high percentage is used in initiating radicals. Thermal activation of the same or similar systems can be achieved only by a large increase in the overall molecular energy of the environment; hence ultra-violet curing is likely to be more efficient than thermal methods for inducing polymerisation.
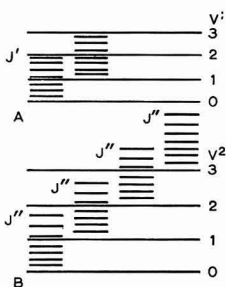

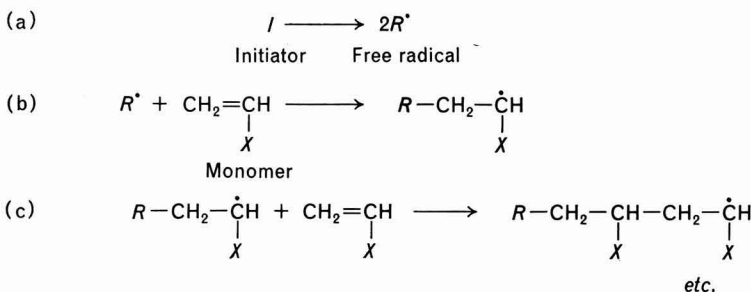Fig. 1a. Energy level diagram for a molecule

Absorption problems posed by titanium dioxide

The use of UV-curing poses a major problem for systems in which titanium dioxide is used. Titanium dioxide has only small infrared absorption characteristics compared with its UV-absorption properties. As a result, it will allow the passage of infrared into the polymer matrix, but not the majority of the UV radiation, which will be almost totally absorbed in the upper region of the paint system. Thus, the efficiency of the UV-curing system will be seriously reduced.

Formulation

Ref. 1

A UV-curing system consists essentially of an oligomer, a polyfunctional monomer, a monofunctional monomer, photoinitiator, a synergist, and pigment.

The oligomer or "prepolymer" can be an unsaturated polyester, an isocyanate-modified acrylic, or an epoxy acrylic, and should be of relatively low molecular weight. The low molecular weight is necessary because no conventional solvents are present in the formulation, and as a result it is not possible to incorporate a high molecular weight polymer because of the associated high viscosity and consequent flow problems. The polyfunctional monomer and monofunctional monomer are chosen to reduce the viscosity of the system; when the system is cured, they will copolymerise to form part of the matrix. Not only is the total concentration of polyfunctional and monofunctional monomer important, but also the ratio of one to the other, since this variable will have a marked effect on viscosity and curing time. The photoinitiator is of vital importance because no matter how potentially reactive the matrix is, it will not crosslink if free radicals are not produced. Production of free radicals or excited states by the photoinitiator is a function of the wavelength of the incident radiation, and if the pigment incorporated in the system is screening out radiation of the vital wavelengths then the system will not cure.

The mode of action of the synergist has not been fully elucidated, although Dr Ledwith's paper[1] deals admirably with the current thinking on this problem. However, it is well known that the incorporation of an amine (synergist) with an aromatic carbonyl compound can markedly improve the efficiency of vinyl polymerisation, and such a mixture is far more effective than photoinitiator alone. The synergists used in UV technology are amines, which are oxidised to give rise to free radicals via an excited complex ("exciplex"). The importance of "exciplex" formation with respect to systems containing titanium dioxide stems from the fact that the

Fig. 2. Free-radical chain mechanism

redox potential for the photo-reduction of an aromatic carbonyl compound by the synergist is in the region of 1-2 electron volts. This energy requirement can easily be supplied by radiation of the blue end of the visible spectrum e.g. 450 nm (2.76 ev); 500 nm (2.48 ev). As the absorption edge of rutile type TiO_2 lies at 420 nm, the advantage of such photoinitiator systems are obvious.

Mode of action of a photoinitiator

Once a radical reaction has been started, it often proceeds at great speed owing to the propagation of fast chain reactions, but free radicals must first of all be formed and in the coatings

phenone or 2-chloro thioxanthone or a benzoin alkyl ether. The carbonyl compound initiates polymerisation via its triplet state (Fig. 3) and the benzoin alkyl ether via homolytic fission of which the precursor could be excited or triplet.

In order to form radicals, the photoinitiators benzophenone and the benzoin alkyl ethers must firstly pass through an excited state. (The energy-state diagram for benzophenone is shown in Fig. 5.) However, in order that the excited states may be formed, the longest wavelength at which these two compounds can be irradiated is approximately 406 nm for benzoin butyl ether and 378 nm for benzophenone; this can be understood by reference to their absorption spectra (see Fig. 6).
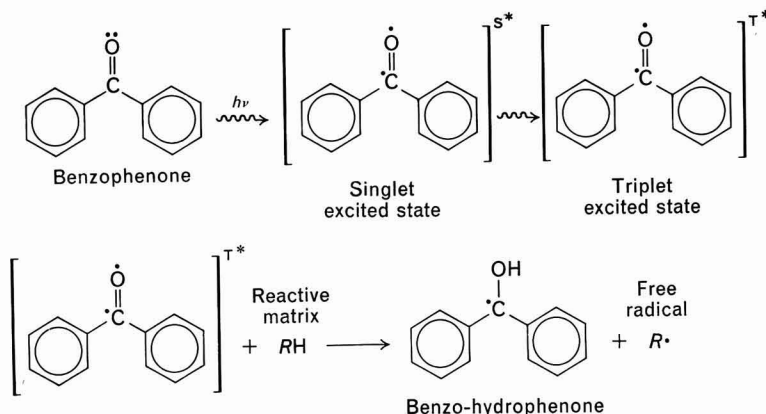
Fig. 3. The role of benzophenone as a photoinitiator
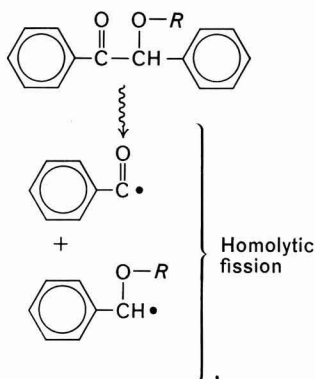
Fig. 4. The role of a benzoin alkyl ether as a photoinitiator

industry a class of compounds called "photoinitiators" is used to provide a source of primary radicals. Such compounds will furnish radicals with comparative ease when irradiated with ultraviolet light (Fig. 2). All the photoinitiator systems used at present include either a carbonyl compound e.g. benzo-
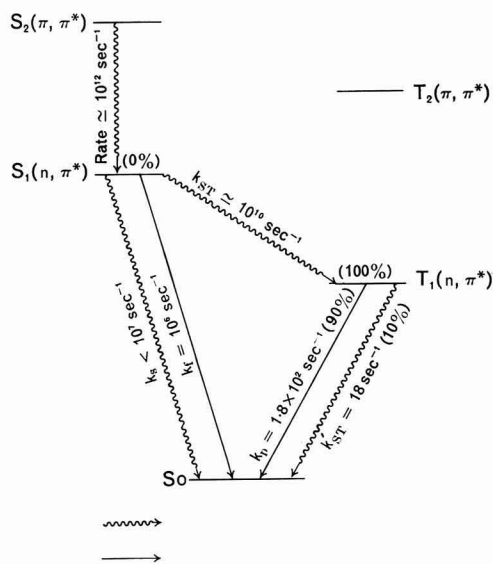
Fig. 5. Energy state diagram for benzophenone   *[See key overleaf*

Key

Radiationless processes (i.e. relaxation processes which are not accompanied by the emission of radiation)

Relaxation processes accompanied by fluorescence or phosphorescence

After radiation of the initiator, the excited electron occupying the (π, π^*) orbital at the S_2 level relaxes to the S_1 level of the (n, π^*) orbital. It is now in a position to (i) relax to the ground state S_0 by processes of internal conversion or fluorescence, or (ii) undergo intersystem crossing to the triplet state in the (n, π^*) orbital. The rate constant for intersystem crossing k_{st} is much greater than the rates for fluorescence k_f and internal conversion k_s.

$$k_{st} \gg k_f \ or \ k_s$$

Thus nearly 100% triplet is formed. The lifetime for the triplet is governed by the rate constant for phosphorescence k_p and by k'_{st} the rate for intersystem crossing, but $k_p = 10k'_{st}$, so the lifetime of the excited state is governed essentially by the rate of phosphorescence, which is slow.
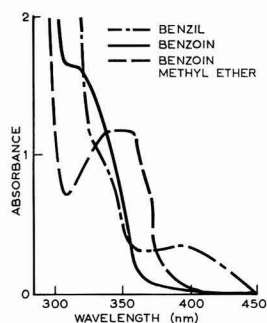
Fig. 6. UV absorption spectrum of photoinitiators

Table 1

Pigment types used in transmission experiments

Rutile pigment	Mean crystal size (μm)	Anatase pigment	Mean crystal size (μm)
R-FC2 94.6% TIO$_2$	0.17	A-PP2	0.15
R-HD2 95.0% TIO$_2$	0.20		
76/2	0.26	M 199/1	0.05

Table 2

Percentage UV transmission by a 1μm film pigmented at 10% PVC

Wavelength (nm)	Pigment				
	R-FC2	R-HD2	76/2	A-PP2	M199/1
350				31·0	42·5
360	20·3	27·0	39·0	42·0	59·0
370	23·0	31·0	42·0	66·0	77·0
380	31·5	37·0	46·0	80·0	88·0
390	47·5	51·0	58·0	85·0	92·0
400	69·0	70·0	75·0	86·0	94·0

Table 3

*Percentage UV transmission by a 1μm film pigmented at 20% PVC*

Wavelength (nm)	Pigment				
	R-FC2	R-HD2	76/2	A-PP2	M199/1
350				28·0	28·0
360	4·0	5·5	11·0	31·0	48·0
370	6·0	8·0	14·0	54·5	68·5
380	13·0	14·0	20·0	72·5	84·0
390	29·5	29·5	35·0	78·5	89·0
400	54·0	54·0	57·0	81·0	90·0

Scattering properties of titanium dioxide

As long as a UV-curing system contains only oligomer, monomer, photoinitiator and a pigment which does not absorb strongly in the UV region, then a fast and satisfactory cure will be obtained (providing, of course, the system is suitably reactive). When titanium dioxide is present above a particular concentration then there is serious reduction in the rate of cure of the system. Reference to Fig. 7 will explain this. At 400 nm, rutile-type titanium dioxide is seen to absorb very strongly and at 380 nm, the anatase grade also has a strong absorption—that is, the activating wavelengths for both benzophenone and benzoin alkyl ether are being strongly absorbed. At the high pigmentations required for printing inks and roller-coatings (pigment : binder ratios of at least 0.8 : 1), therefore, it is surprising that systems containing titanium dioxide can cure at all.
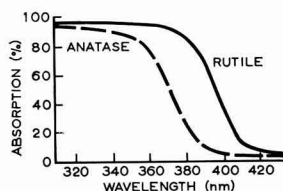
Fig. 7. Absorption spectra for rutile and anatase titanium dioxide

Three years ago, the author examined a very simple UV-curing system. It consisted of pentaerythritol tetra-acrylate, triethanolamine, titanium dioxide and photoinitiator. The coating was subjected to a low-powered UV lamp, and found to cure in less than one second. Adhesion was poor, but it seemed that the film had cured throughout. Since that time, many formulations of UV-curing systems have been examined and it is now possible to achieve an adequate through-cure in a titanium dioxide pigmented system at film weight 0.15 kg m^{-2} when passed under a 1.2 kW lamp (80 W cm^{-1}) at 0.2 m s^{-1}.

The reason for this is that although titanium dioxide strongly absorbs radiation in the UV region of the electromagnetic spectrum some UV radiation is transmitted through the pigmented film, Table 4. The effect of this may be optimised by careful TiO$_2$ selection, choice of oligomer, monomer and photoinitiator.

The opacifying properties of a paint film are related to the way in which it will scatter visible radiation impinging upon its surface. This in turn is a function of the ratio of the

refractive indices of titanium dioxide and polymer, and also the crystal size of the pigment. The crystal size is important because Mie theory shows that a titanium dioxide crystal of a particular diameter will scatter predominantly visible radiation of a particular wavelength: hence the reason for grades of titanium dioxide with small crystal size exhibiting blue undertones and coarser grades exhibiting brown undertones. Titanium dioxide manufacturers usually design their pigments to give maximum scattering in the green region of the visible spectrum. This demands a range of crystal size between approximately 0.17 and 0.26 μm. The pigment manufacturer, depending on the undertone required, will design his pigment so that the mean crystal size lies within this range. Thus different commercial grades of pigment may differ in their mean crystal size.

It so happens that the scattering of UV light is also dependent on the crystal size of the pigment. Experiments have shown that the degree of UV penetration into titanium dioxide pigmented systems is dependent on the crystal size of the pigment. In this work, three rutile and two anatase pigments were examined in an alkyd/amino medium at two pigment volume concentrations (10 and 20 per cent). The alkyd/amino medium was chosen because it did not absorb UV radiation significantly at the wavelengths under consideration: absorption by the medium would have complicated interpretation of the results. The paints were applied to silica panels by a spinning technique and the thickness of the paint film was determined by an X-ray flourescence method. The transmission of UV radiation through the paint films was then measured and the results interpolated to within 1 μm. Table 1 indicates the types of pigment used and Tables 2 and 3 show the transmission values at 10 and 20 per cent PVC. The results show that:

(i) for rutile pigments, grades with large crystal size are less efficient scatterers of UV radiation than with small crystals. Thus, grades with a large crystal size allow greater penetration of UV radiation;

(ii) for anatase pigments, grades with large crystal size are more efficient scatterers of UV radiation than grades with small crystal size, so that it will be the grades with large crystal size which will allow less penetration of UV radiation.
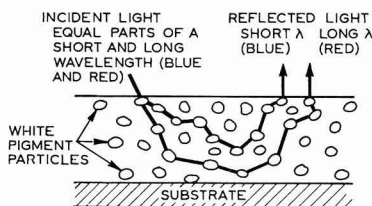

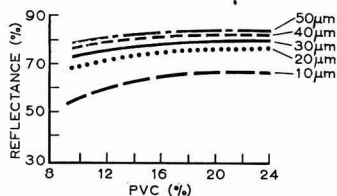Fig. 8. Scattering of light by white paint

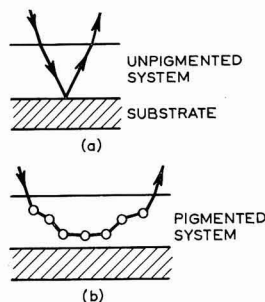Fig. 9. Opacity versus PVC for various film thicknesses

Fig. 10. Scattering of UV radiation by titanium dioxide at low PVC

At the present time it is uncertain whether this increase in transmission with crystal size is sufficiently large to produce in practice any more rapid rate of cure with increasing crystal size. Experiments carried out in the laboratory have shown that differences in curing rates between systems containing pigments of differing crystal size are difficult to demonstrate consistently. This may be because of the difficulty in applying thin films of a constant thickness. It could also be that there is more than sufficient UV penetration even with the small crystal size to effect the complete polymerisation of a "thin" (2 μm) film. However, a pigment with a large crystal size at a high PVC will give a higher visual opacity in a thin film than one with a small crystal size at the same PVC; it is possible, in fact, to use as much as 10 per cent less pigment of the larger crystal size and still obtain the same visual opacity shown by the pigment with the small crystal size. This factor, coupled with intrinsically lower UV-scattering properties of the larger cystal size should significantly increase UV penetration.

The fraction of UV radiation transmitted through a 20μm film has been calculated. The percentage transmission at 400 nm is several orders of magnitude greater than at 380 nm (Table 4).

Table 4
UV transmission through a 20μm film

Wave-length (nm)	Pigment grade and crystal size			
	R–FC2 (0.17μm)	R–HD2 (0.20μm)	76/2 (0.26μm)	A–PP2 (0.15μm)
	Percentage transmission			
360	6.6×10^{-16}	1.9×10^{-13}	2.3×10^{-10}	9.8×10^{-9}
380	8.7×10^{-10}	2.3×10^{-9}	3.7×10^{-8}	6.4×10^{-2}
400	7.4×10^{-3}	8.6×10^{-3}	1.2×10^{-2}	2.7×10^{-1}

In addition to the use of pigments with large crystal size, there are other ways by which the opacity may be increased without detriment to UV penetration. One way is to reduce the pigmentation and apply a thicker film. It has long been known that a thick film pigmented at, say, x PVC will give a higher opacity than a film of half this thickness pigmented at $2x$ PVC. What is not common knowledge, however, is that the thicker film with a lower PVC will transmit the same amount of UV radiation. The relationship between opacity and PVC is shown in Fig. 9. If a 10μm film at 20 per cent PVC is compared with a 20μm film at 10 per cent PVC, the opacities measured as a function of green light reflectance are 64 and 69.5 per cent, respectively; for a 10μm film at 22 per cent PVC and a 20μm film at 11 per cent PVC, the reflections are

64 and 71 per cent. From the trend in Fig. 9, it would appear that even greater advantages could be obtained if this principle were operated in the region 5-10μm. Of course there is some increase in cost using a thicker film, but the formulator may have to incorporate pigment at a lower PVC than he originally intended, because of flow problems, and thus have to apply a thicker film.

A lower PVC than originally intended might, therefore, be considered, and a finish having a higher gloss and less prone to "rivelling" (see below) should be obtained.

Low PVC sensitisation

Although no systematic work has been carried out on this phenomenon, it is worthwhile commenting on several reports[2] that titanium dioxide may act as a photosensitiser when incorporated into suitable photosensitive polymers at low PVCs.

It is observed that when titanium dioxide is incorporated into a photosensitive polymer at <2 per cent PVC and subjected to UV irradiation, the rate of cure of this system appears to be faster than for an unpigmented one. It is a well-established fact that titanium dioxide is a semi-conductor and under UV irradiation its surface is activated in such a way that it will react with isopropanol in the presence of oxygen to produce acetone. However, relative to the speed of photo-initiation, this process seems to be slow, and would not appear to explain this phenomenon in UV-curing systems.

The correct explanation is thought to be that due to scattering of UV radiation in a low PVC system, the "path-length" of the radiation is longer in the pigmented system than than it is in the unpigmented one. The PVC of such a system is of course, very low (less than two per cent). A better understanding of the situation is gained by reference to Fig. 10.

In the unpigmented system (a), the UV radiation is reflected from the substrate and directly out of the system. In system (b), the scattering properties of the titanium dioxide increase the path length of UV radiation passing through the system. Because of this phenomenon, it might be possible to use small amounts of titanium dioxide in coloured systems, particularly in those for screen printing, in order to assist the curing of these systems at high film weights.

Anatase pigments

If the absorption spectra and UV penetration results for the two anatase pigments are considered, it is quite obvious that UV penetration is considerably higher for anatase grades than it is for rutile grades. Anatase pigments are not recommended for UV systems, however, for two reasons:

1. Anatase pigment has a lower refractive index than rutile and thus it confers less opacity at the same PVC.

2. It has a smaller average crystal size. This is due to the greater thermodynamic stability of the rutile grade compared with anatase. In order to increase the crystal size of anatase pigments, it is necessary to calcine at higher temperatures, and this unfortunately results in the conversion of the anatase crystal to rutile.

The overall result is that more anatase pigment will be required than rutile pigment to give equal visual opacity in a roller-coating or printing ink and as the crystal sizes of anatase pigments are so much smaller than rutile grades, their

associated surface area per unit volume will be proportionally higher. This will obviously result in a higher viscosity in a system containing anatase pigments, necessitating the addition of more oligomer, polyfunctional monomer or mono-functional monomer. Usually, it is the monofunctional monomer which needs to be increased.

General rheological considerations

The attainment of good flow in a high solids system is proving to be more difficult than obtaining a satisfactory fast cure; it is a problem which applies particularly to systems pigmented with titanium dioxide. In such systems definite advantages such as lower yield values, may be obtained with the use of a lightly coated, silicone treated, large crystal size titanium dioxide grade. Such a pigment is Tioxide R-TC2 which is manufactured by the chloride route. A large crystal size grade has a smaller surface area than a small crystal size grade (coating levels being equal) per unit weight (see Appendix) thus it should exercise a lower medium demand. The light coating is also important in affecting a lower medium demand, and coupled with the silicone addition maintaining a low moisture content. The presence of moisture in the pigment above a particular percentage has been shown to increase the thixotropy of the system. This effect of moisture content probably applies to the monomer as well as the pigment. The most serious flow problems have been encountered in white-base coats for two piece cans, where a few seconds elapse after coating before curing. However, with improvements in application techniques the problem may be solved. In the printing ink area the problem of flow is less serious. The concern in this area is with the consistency of the ink, and the "stiffness" and "tack" required for an offset litho ink can and has been achieved with UV systems. The pigment which is recommended for this type of work is Tioxide R-HD2. In some cases ink manufacturers have obtained satisfactory inks by blending different grades of titanium dioxide.

The introduction of lower viscosity oligomers is also making it somewhat easier for the formulator. This has been achieved in some cases by improvement of the earlier oligomer systems by chemical modification such as the esterification of OH groups in epoxy-acrylate oligomers. Improved flow is also obtained by the addition of conventional flow agents such as cellulose acetate butyrate and surfactants of the polyoxy-ethylated nonylphenol type.

Surface wrinkling (rivelling)

One of the problems with white systems is their susceptibility to wrinkling on the surface during the polymerisation process. This is a difficult phenomenon to examine as there appear to be several variables which can cause it. Essentially, rivelling is probably due to the surface of the system curing more quickly than its interior. This sets up stresses, which result in the formation of microscopic convolutions on the surface of the ink or paint. The problem is particularly relevant to systems containing titanium dioxide, because of the poor UV pene-tration, and is more troublesome at high film weights and at high pigment-to-binder ratios. There is evidence that incorrect selection of monofunctional and polyfunctional monomer, as well as photoinitiator, can also affect the degree of rivelling. Table 5 shows the effect of pigment content and film thickness on rivelling, when the system is based on a particular formula (Formula *1*, Table 6). However, modification of the for-mulations to give Formula *2* (Table 6) produces no rivelling. Formulations *1* and *2* are pigmented with Tioxide R-TC2 and are based on a mixture of six parts vinyl ester (Derakane XD

Table 5

Effect of pigment content, initiator and film thickness on rivelling
Formulation 1

Pigment/	Film thickness (μm)				
binder ratio	6	12	25	36	50
1·2 : 1	R*	R	R	R	R
1·0 : 1	R	R	R	R	R
0·8 : 1	—	—	R	R	R
0·6 : 1	—	—	—	R	R
0·4 : 1	—	—	—	—	R

*R = Rivelling occurred on curing

Formulation 2

No rivelling apparent

Table 6

Roller-coating formulations (Pigment/binder ratio = 1.2:1)

	1	2
	(Parts by weight)	
R-TC2	100	100
Derakane XD8008	50	50
Sartomer SR351	17	17
Sartomer SR432	17	17
Trigonal 15	4·2	—
Trigonal 14	—	2·1
2-methyl anthraquinone	—	2·1

Sartomer is the registered trade mark of Ancomer (UK) Ltd.
Derakane is the registered trade mark of Dow Chemical Co.

8008), two parts trimethylol propane triacrylate (Sartomer SR 351) and two parts of benzyl acrylate (Sartomer SR 432) as medium. The initiator in formulation *1* is "Trigonal 15", and in *2* a mixture of "Trigonal 14" and 2-methyl anthraquinone. In both cases, the initiator was present at 5 per cent by weight (on medium). The effect of using a mixture of photoinitiators is an interesting one and merits amplification. Some photoinitiators are wavelength-sensitive, which means that they will give rise to a higher quantum yield of excited triplet states at particular wavelengths. A mixture of photoinitiators incorporated into a printing ink is more likely, therefore, to be sensitive to a wide band of wavelengths than only one photoinitiator. This can result in a faster cure, or a different degree of through-cure. It has been found consistently in the author's laboratories that a mixture of "Trigonal 14" and 2-methyl anthraquinone will always give a faster cure and impart greater scuff resistance to the cured film than will "Trigonal 14" alone. It might be argued that, if the theory that wrinkling is due to a too rapid surface cure is correct, then the mixture of "Trigonal 14" and 2-methyl anthraquinone should be worse than "Trigonal 14" alone. This is an over-simplification of the situation, because not only are the photoinitiators different chemically, but they also react differently. They will have different rates of reaction with the monomer, oligomer and also with oxygen. It has been found that the introduction of a new photoinitiator can have a more far reaching effect than altering the period of irradiation.

It is also possible to avoid rivelling by altering the content and type of monomer. Table 8 shows gloss results for films of approximately 12 μm thickness prepared from coatings pig-

mented at a pigment : binder ratio of 1 : 1 with both small and large crystal pigments. The basic formulation of the coatings is given in Table 7.

Table 7

Basic formulation of coating used to study rivelling (see Table 8)

Titanium dioxide pigment	100
Vinyl Ester	60
Polyfunctional monomer	20
Monofunctional monomer	20
Trigonal 15	5

Table 8

Effect of monomer type on rivelling

Polyfunctional monomer	TiO₂ crystal size	Monofunctional monomer		
		SR 220	SR 432	Butyl acrylate
Sartomer SR 351	Large	96	8	93
T.M.P. triacrylate	Small	92	4	83
Sartomer SR 238	Large	65	7	71
1:6 Hexane diol diacrylate	Small	38	5	76
Sartomer SR 247	Large	86	9	87
Neopentyl glycol diacrylate	Small	90	26	81

The low gloss values with benzyl acrylate (Sartomer SR432) are due to bad rivelling of the paint film. Rivelling to a lesser extent is also apparent in all coatings employing 1,6 hexane diol diacrylate (Sartomer SR238) as polyfunctional monomer. SR220 is cyclohexyl acrylate.

Since the bulk of this work was done, experiments using benzil and morpholine[3] have been carried out. UV systems pigmented at 20 per cent PVC and applied at a thickness of 50 μm have been cured to a scuff resistance level in less than one second using radiation which lies outside the UV absorption spectrum, there was no sign of rivelling. This convincing demonstration of the superiority of "exciplex" photoinitiation over more conventional photoinitiators in systems pigmented with titanium dioxide could lead to significant developments in the use of UV in white surface coatings.

In this paper, reference has been made to several ways of improving the performance of systems pigmented with titanium dioxide. Each by itself may appear to have a small effect, but together they can make a significant contribution to the performance of the final system and in a particularly difficult system could make the difference between "pass" and "failure".

UV-curing is still in its infancy and much work remains to be done in all its aspects. The UV-absorption characteristics of titanium dioxide cannot be altered, of course, and will continue to challenge the formulator to his utmost in an effort to obtain a satisfactory paint or ink. It is hoped that the information presented here will be of some assistance to him in achieving that goal.

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Appendix

Surface area calculation

Surface diameter (cm) $= d$

Density of sphere (g m^3) $= \rho$

$\therefore$ Volume of sphere $= \pi d^2/6$ and area $= \pi d^2$

$\therefore$ Weight of single sphere (crystal) $= \pi\rho d^3/6$

so that the number of spheres per gramme $= 6/\pi\rho d^3$

and, therefore, the total surface area per gramme (cm^2 g^{-1})
$= 6\pi d^2/\pi\rho d^3 = 6/\rho d$

Painting metal bridges—historical and current trends

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Summary

The development of metal bridges is traced from the construction of the iron-chain "Wynch Bridge" in 1741 and the "Iron Bridge" in 1779 to the most recent road bridges under construction. The simultaneous development of painting and protective systems is described.

Keywords

Types and classes of structures or surfaces to be coated

steel

Le peinturage des ponts métalliques—tendances historiques et actuelles

Résumé

On trace l'évolution des ponts métalliques à partir de la construction en 1741 du "Wynch Bridge" à chaînes de fer et du "Ironbridge" en 1779 jusqu'aux ponts routiers de construction la plus récente. On discute le développement simultané des systèmes de peintures et de protection.

Metallbrückenanstrich—Geschichtliche und Gegenwärtige Trends

Zusammenfassung

Die Entwicklung von Metallbrücken wird skizziert, beginnend mit der Konstruktion im Jahre 1741 der Eisenketten—"Wynch Bridge" und im Jahre 1779 der "Ironbridge" bis zu den allerneuesten, noch unter Konstruktion befindlichen Strassenbrücken. Es wird die gleichlaufende Entwicklung von Anstrich und Schutzsystemen beschrieben.

Among the achievements of civil engineering, the bridge has played a major role in shaping present day civilisation. Many of the world's greatest cities, for example, Rome, San Francisco and Sydney, could not have developed in their present forms without the bridge. It is well known that masonry bridges have survived for centuries, but as the need developed for less massive foundations, lighter and longer spans, and more rapid construction, engineers looked at alternative materials and, as a result, ferrous metals have emerged as the most suitable, in spite of their one great disadvantage—corrosion. To overcome this problem a technology of protective treatment has gradually developed. Progress in this technology can readily be demonstrated by reviewing selected bridges constructed in the United Kingdom during the last two centuries.

It is a fitting coincidence that what was probably the first iron-chain bridge in Britain was "Wynch Bridge" across the River Tees, because one of the largest bridges now being built in this country, and one of considerable significance in the practice of bridge painting, is also across the Tees.

Wynch Bridge was built in 1741 by miners. It had only one hand chain. An interesting account is given in Hutchinson's 1785 "History of Durham" and to quote:

"the traveller experiences all the tremulous motion of the chain and sees himself suspended over a roaring gulph on a restless gangway to which few strangers dare trust themselves".

Wynch Bridge collapsed in 1802, killing two people. The collapse was attributed to corrosion of the chains and, whether true or false, this provides an ominous reminder of the importance of corrosion control.

It was not until 1755 that serious consideration was given to building a bridge with iron. The bridge concerned was partly fabricated in a builder's yard at Lyons, but funds and courage ran short and eventually a timber bridge was built.

Ref. 1

The first bridge in the world to be made of iron successfully was Ironbridge[1] in Shropshire, which still spans the River Severn at Coalbrookdale, and which is now preserved as an ancient monument. This bridge was designed by Thomas Pritchard and was erected in 1779.

Coalbrookdale was the centre of a thriving iron-making community. When a scheme was put forward to replace the Coalbrookdale ferry by a bridge, it was not surprising that iron was considered as a suitable material. The ironmasters of that day had an almost fanatical faith in the new material developed by smelting iron ore with coke instead of charcoal. Some were deemed to be "iron-mad", who forecast that ships and even houses would be made of iron.

Abraham Darby III (a grandson of Abraham Darby, who in 1709 had discovered the new smelting technique) and a partner submitted an estimate of £6000 for the bridge. Darby lost money on the project, but the publicity was adequate compensation and in 1787, he received a gold medal from the Royal Society of Arts.

Ironbridge has a main arched span 31 metres long and 15 metres high. A total of 384.6 tonnes of iron were used in

the bridge. Even the deck is formed of flat cast iron plates 50mm thick overlaid with slag and clay. All parts, except the railings, were open cast in sand, and construction took three months.

It is doubtful whether at this time any coating was applied to protect the iron-work from corrosion. The first record of protective treatment appears in 1788 when varnish was applied to the ironwork. The varnish was supplied from Lord Dundonald's British Tar Company, which had kilns at the nearby Calcutt and Benthall iron works.

The North Bridge, Halifax, constructed in 1870 may be taken as the second example of a cast-iron bridge. Whilst not making any particular claims to fame, this bridge provides an interesting picture of bridge painting over the past 100 years. North Bridge occupies a prominent position near the town centre of Halifax and within sight of the Town Hall, and more consideration has been given to maintaining the appearance of this bridge than many of its counterparts in less conspicuous positions. Regular painting has meant that successive coats of paint were applied on top of the existing system.
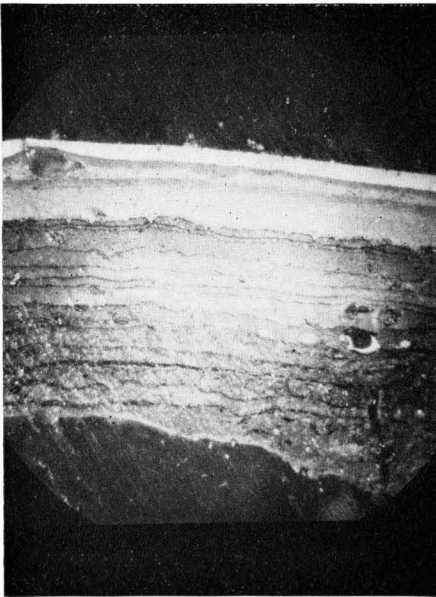

Fig. 1. A section through a paint flake removed from the North Bridge, Halifax, showing the coats applied during 102 years

It is estimated that 1.6 tonnes of paint had been applied to the two outer girders and parapets of this bridge before old age and gravity overcame adhesion and cleaning back to bare metal became necessary in 1973.

In the century which followed the construction of Ironbridge, technical developments in structural iron were considerable. In 1784 Cort announced a process for producing wrought iron from pig iron by means of the puddling furnace. It was not, however, until the middle of the nineteenth century that full use was made of this invention. Wrought iron has a tensile strength almost three times that of cast iron and it enabled bridges to be built with members in tension (for example, suspension) as well as in compression.

Two fine examples of the use of wrought iron are Telford's suspension bridge across the Menai Straits to Anglesey, having a main span of 176 metres, and his smaller bridge (100 metres) of similar design at Conway; both of these were completed in 1826. Telford employed a flat wrought iron link "of the best Shropshire hammered iron" for the suspension chains of these bridges. The Menai Bridge and its approaches were constructed at a cost of £120 000.

Ref. 2

Telford's original design (1810) was for an arched, cast-iron bridge across the Menai Straits, but in 1814 he proposed the present wrought-iron suspension bridge. Work began in 1817 and contemporary reports indicate great public interest in the construction works. Crowds would assemble to watch progress and cheer as major items were erected. A band played as the great chains were hauled into place and free beer was provided for the workmen. Telford did recognise the importance of protection against corrosion. Before assembly, all parts of the chains were cleaned, dipped in boiling linseed oil and heated whilst draining. They were then primed[2] with a white lead-in-oil paint. It is reported that this practice intrigued the spectators and a romanticised interpretation appears in "Alice through the Looking Glass" with a reference by the White Knight when he tells Alice:

"I heard him then for I had just completed my design
To keep the Menai Bridge from rust by boiling it in wine"

Precisely what the boiling linseed oil was expected to do seems shrouded in mystery. Recent tests using accelerated conditions of salt spray have shown that whilst it does not appear to detract from the corrosion inhibiting properties of a subsequent coat of white lead-in-oil paint, it does not provide any obvious advantage. In fact, shortly before the Menai Bridge project, the Seguin brothers in France had used the technique with unfortunate results, for the high temperature of the oil adversely affected the strength of wires. However, modifications of the hot-oil technique continued to be used for at least another 75 years.

Shortly before the 1939-45 war, the wrought iron chains of the Menai Bridge were replaced by steel chains of the same design. The chains at Conway still have Telford's original wrought-iron links.

The underside of both bridges has always been protected by black bitumen, as was traditional.

The use of wrought iron as a structural material probably reached its zenith with the opening in 1859 of Brunel's Royal Albert Bridge over the River Tamar at Saltash. It was during the construction of this bridge that Bessemer invented his converter (1856) by which mild steel could be economically produced. This material was subsequently to replace wrought iron.

In 1865 the open-hearth process of Martin and Siemens was introduced and formed the basis of structural steel production until recent years, when the electric arc furnace largely replaced it.

The production of steel on a commercial scale commenced in 1866 and a few years later it was used for bridges abroad, but in Britain the Board of Trade prohibited its use for bridge construction until 1877.

By the time that the next great bridge was to be designed, the use of steel was well established abroad and in 1880

Fowler and Baker presented their plans for a railway bridge across the River Forth.

The original plans for a railway bridge across the River Forth were made by Thomas Bouch, and foundation works had already started when his bridge across the River Tay collapsed. Needless to say, work at the River Forth site stopped abruptly. Sir John Fowler and Benjamin Baker (later knighted for his work) submitted designs for the bridge which stands at present to the interested companies, *viz.* North British, North Eastern, Midland and Great Northern Railway Companies. In 1882, the contract was awarded.

Baker's use of steel for the Forth Bridge marked the beginning of a new age of steel by demonstrating its potential. The Forth Bridge was Britain's first bridge of open-hearth steel.

Ref. 3

The Forth Bridge is of cantilever design, having three spans of 521 metres each[3]. The total length of the structure is 2.53 kilometres. About 55 000 tonnes of steel were used and 6.5 million rivets, weighing a total of 4270 tonnes, were used as fasteners. The surface area for painting is 552 720m².

The bridge took eight years to build and was opened on 4 March 1890. It was the largest bridge in the world. During the years of peak construction, 4600 men were employed and the cost of construction was £3 177 206. There were 57 fatal accidents. Safety boats saved at least eight people who fell into the river plus 8000 caps and other garments.

The steel tubes for its construction were fabricated at Queensferry, where the contractor, Tancred, Arrol and Company, installed special steel rolling equipment specifically for the job.

Records show that natural exposure testing of three years duration was used to select a paint system for this bridge. Several paint companies took part in these trials and the firm which was approved by Benjamin Baker at that time has been the supplier of coatings for the bridge ever since.

Before erection, all steel was scraped, wire brushed and coated with boiled linseed oil applied whilst hot. This was followed by a coat of red lead in oil, applied either before or after erection. A second coat of red lead was applied after erection, followed by one coat of "Dark chocolate" red oxide primer and one coat of "Persian red" (or "Bright Indian red") red oxide finishing paint.

The interior of the tubes was painted with one coat of red lead in oil followed by two coats of white lead in oil.

A total of 161 506 litres of "paint oils" and 254 tonnes of paint were supplied to the site during construction.

The Forth Bridge is invariably cited when the subject of maintenance painting of large structures arises, because for this bridge, maintenance painting is a continuous process, employing 20 to 24 men. Permanent employment is possible since in periods of inclement weather the gangs are able to paint inside the huge tubes. Externally, 56 tonnes of red-oxide paint per coat are applied at a rate of about 17 tonnes per year, so that it takes three to four years to complete one cycle. When it is considered that the original plans were for a structure of "limited life", it speaks highly of the protective system that in 1965 a report was made to Parliament

Fig. 2. Typical erosion of white lead paint BS2525 during 10-15 years of exposure in mild industrial conditions. Patches of the primer are beginning to become visible

stating the structure to be sound and suitable for continued service.

At this point, to digress slightly, it is interesting to review the status of the painter. From earliest times, he had been held in high regard as a craftsman, but by the 12th century, long after the firm establishment of oil paints, the painter had assumed a more humble role in society. At the time of construction of the Menai Bridge in 1824, a painter was no longer considered a skilled worker and would receive between 11.5p (2/4d) and 14p (2/9d) per day, compared with the 36.5p (7/4d) to 39p (7/9d) per day paid to skilled workers, such as blacksmiths. Sixty years later (on the Forth Railway Bridge project, for example), he could expect 22.5p (4/6d) for a 12-hour day compared with 40p (8/0d) to 60p (12/0d) for a riveter.

Steel has maintained its position as an important and economically competitive material for bridge construction, but even as the first trains crossed the Forth Bridge, a new building material, reinforced concrete, was coming into use. The first bridge to be constructed of reinforced concrete (at Satterthwaite, Lancs) was completed in 1902.

In 1906 a British Standard, BS15, was introduced, originally entitled "Specification for structural steel for bridges and general building construction".

It was still several years before it was generally appreciated that mild steel could corrode more rapidly than wrought or cast iron and, therefore, required more careful protection. In many instances, the full importance of surface preparation was not realised by the structural engineer (or his paint supplier). The use of red lead in oil had been the standard practice as a protective treatment for structural metalwork

for years. This material is so tolerant of inadequate or even non-existent surface preparation that this latter aspect of painting practice had been largely overlooked. Improved corrosion resistance and shorter re-coating times were among the first demands of the developing construction industry. Although the academics had some understanding of the theory of corrosion, few (if any) were employed in the paint industry. Paint chemists were still something of a curiosity, consequently the development of paints which inhibited corrosion was slow. The situation was complicated by a feed-back of misleading information from some fabricators, who still preferred to mix their own lead-in-oil paints to secret formulations of doubtful reproducibility, and by the inflexible ideas of a few engineers who continued to specify their own cherished protective systems that had been "proven" by personal experience, often under conditions totally irrelevant to the project in hand.

Metal primers containing red oxide of iron were in use on bridges by the middle of the 19th century and similar paints are still in use. Basic lead sulfate was introduced early in the 20th century and at about the same time there was a major improvement in the durability of finishing paints with the introduction of micaceous iron oxide (MIO). The inert nature and flakelike shape of the MIO particle enabled paints containing it to form a protective barrier against environmental attack, which complemented the protection afforded by the corrosion inhibiting primer. With the appearance of zinc chromate primers in the 1930s, the beginning of protective systems as they are known today had arrived.

By 1945, the number of corrosion inhibiting primers available was considerable and the Protective Coatings (Corrosion) Sub-Committee of BISRA decided to set up a Technical Panel to evaluate them. Over 100 primers were
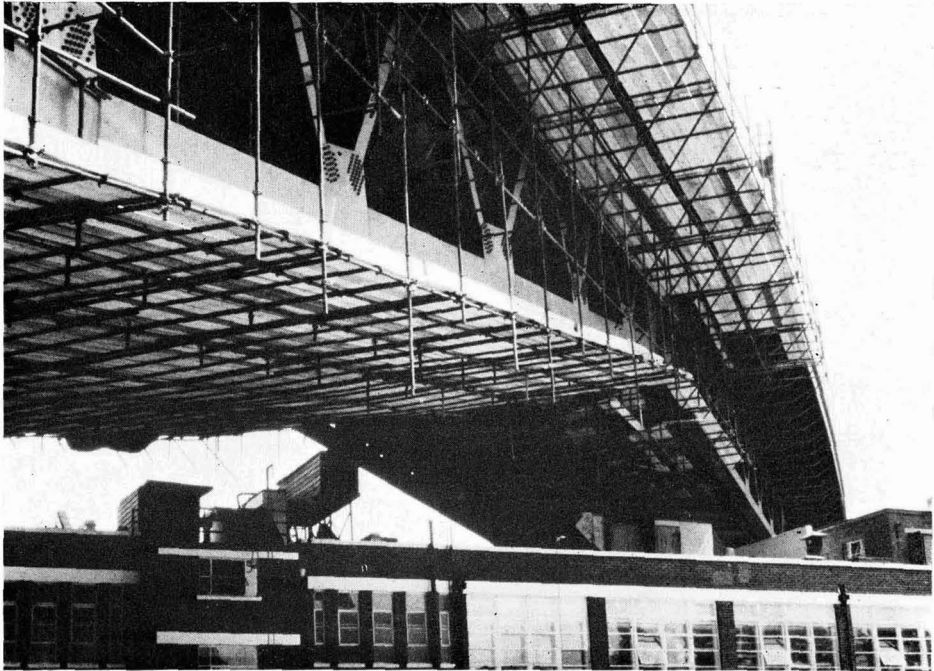

Fig. 3. Example of limited accessibility for maintenance of an urban motorway bridge

tested, some containing blends of two or more pigments. From that time, the development of priming paints became more rapid, and various commercial interests began to influence the construction industry. It is the author's belief in retrospect that the industry owes something to British Railways when it introduced its paint specification scheme in 1949. This was a bold attempt to introduce "horses for courses" and regulate the number of new types of paints being offered to engineers.

With the introduction of motorways to Britain during the 1950s came the need for many new bridges, several of which were to be among the longest in the world at that time. These huge bridges were designed with a projected life of 120 years. It was soon realised that their maintenance could be very expensive and that a first class protective system applied at the time of construction could prove the most economical method of protection over the first 20 years of service, particularly with the arrival of urban motorways, where access for maintenance was often limited.

The Ministry of Transport was among the first to recognise the importance of an environmental study to characterise the nature of the environment in which the bridge would stand and the special environmental conditions which would prevail under wide bridges, where airborne chemical pollutants can lodge on the paintwork and never be washed off by rain. Recognition of these factors resulted in the development of protective systems which were "tailor made" to avoid costly over-specification or even more costly under specification and premature failure. On this basis, the new £9 340 000 Forth Road Bridge, which was opened in September 1964, brought the introduction of a system of metallisation plus paint, which became known as the "Forth Bridge

system" and was used on several other bridges built at that time.

Ref 4

Protection of the Forth Road Bridge[4] called for the blast cleaning of over 29 000 tonnes of exposed steelwork, followed by spraying with metallic zinc. This was coated without delay with a two-pack etch primer, and followed by two coats of zinc chromate and one coat of MIO paint, both in a phenolic medium. Efficient organisation and inspection at the special factory set up for this project no doubt contributed to a significant extent towards the success of the corrosion protection scheme. After erection, a final coat of MIO/phenolic paint was applied.

The benefits of applying as much of the protective system as possible under cover were amply demonstrated by the success of the Forth Bridge project. Work could proceed at times when working in the open would have been impractical.

The next generation of major road bridges were all treated by a system of protection in which all but the top "cosmetic" coats of paint were applied in an enclosed workshop. Typical examples are:

Tinsley viaduct

This is a two-deck structure carrying the M1 and A631 across the Don Valley near Sheffield. This viaduct, completed in 1967, has an external surface area of 119 000m² and is the largest bolted structure in Europe. The protective system involved grit blasting and painting with two coats of a two-pack epoxy zinc-rich primer, followed by two coats
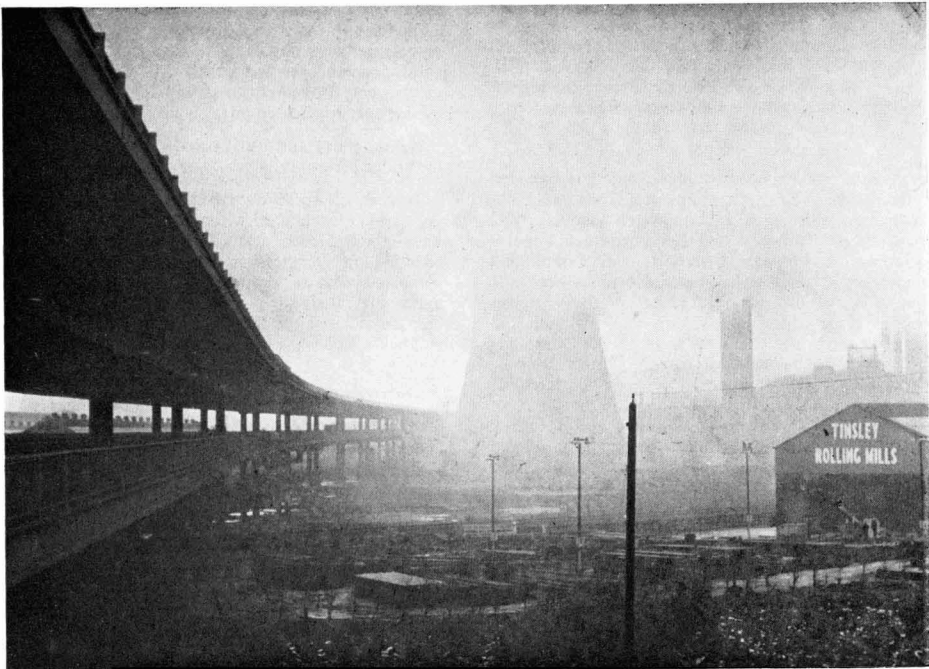

Fig. 4. Corrosive industrial environments produce exacting conditions for protective coatings

of oleoresinous MIO paint. After erection, a further coat of oleoresinous MIO paint was applied. The system is, generally, still sound after eight years in an aggressive industrial environment.

Kirklees viaduct

This steel viaduct, opened in 1973 as part of the M62 trans-Pennine motorway, is of box-girder construction and has an external surface area of 20 000m².

After being grit blasted all steelwork was painted at the works with one coat of blast primer, two coats of an oleoresinous, metallic lead paint, and one coat of MIO tung oil/phenolic paint. After erection had been completed, a further coat of MIO tung oil/phenolic paint was applied, followed by a final coat of a glossy, polyurethane alkyd.

River Hamble M27 Bridge

This is still in course of construction. It is a plate girder bridge with a surface area of 14 000m².

All steelwork has been grit blasted at works and painted with one coat of a two-pack etch primer, one coat of metallic lead, chlorinated rubber paint and one coat of MIO chlorinated rubber paint. After erection, this will be followed by one coat of chlorinated rubber undercoat and one coat of a chlorinated rubber gloss finish.

This trend towards painting at the works was not without its problems for the paint manufacturer. To maintain a scheduled throughput, the fabricator now demanded improved "handleability". Apart from corrosion resistance and general durability, the modern protective paint for bridges had to be sufficiently tough to resist the handling of prefabricated sections weighing many tonnes. It is necessary at times for painters to walk on the primer and undercoats in order to apply successive coats of paint, particularly when painting large prefabricated box girders. The problem was aggravated as it was recognised that relatively thick coats of paint were required to ensure that even the highest peaks of a grit blasted surface were adequately covered.

Ref. 5

To meet these requirements, two-pack materials appeared to be the answer. Long term natural tests, such as those, commenced in 1968 at Loudwater Viaduct (M40 motorway) by the Transport and Road Research Laboratory, compared two-pack materials with traditional and contemporary one-pack materials under realistic conditions of bridge construction. A report[5] on this work was published in 1974. Unfortunately, two-pack materials did not emerge as the bridge engineers panacea. Although they showed the promised resistance to damage during transportation, problems arose with application, recoating, intercoat adhesion and subsequent maintenance. The potential of two-pack materials is recognised, however, and a further series of tests, representing the latest developments offered by industry, was commenced in the Spring of 1974 on the Department of the Environment's model box girders at Teesside. Even as these tests progress, pressure is being brought to bear to exclude lead and chromate anti-corrosive pigments on health and ecological grounds.

Meanwhile, development of one-pack materials to meet the requirements of bridge fabricators has reached a commercially viable stage. An example is the River Tees Bridge, currently in the course of construction. This bridge, nearly two kilometres in length and with a surface area of 118 000m² is of grit blasted steel, painted at works with one coat of a two-pack etch primer and three coats of a zinc phosphate, epoxy ester paint.

After erection, two coats of chlorinated rubber paint will be applied, the final coat being glossy. Situated in an aggressive industrial atmosphere, parts of this huge bridge will stand for approximately three years during construction, before the protective finishing coats can be applied.

The paint industry has had a monopoly of metal bridge protection since the early 19th century. But what of the future? In 1968 the first bridge in Britain to be built of unpainted weathering steel was erected in Wolverhampton. This was the Hordern Road Canal Bridge and it was built of Chromador WQ steel. Weathering steels were first introduced in 1933 in the USA under the name "Corten". As these steels weather, a tightly adherent, compact, oxide film, referred to as "the patina", develops on the surface. Several bridges of unpainted weathering steels have been built, notable examples being those at Ebchester and Crowle, and these bridges are being kept under surveillance.

Another contender for the future is galvanising. In 1974 the first unpainted galvanised bridge to be used in a major road scheme was included in the A19 diversion on Teesside; this was the Stainsby Hall Farm Overbridge, near Yarm. Galvanising was to the requirements of BS 729. The 25 tonnes of steelwork used for this 73 metre bridge were acid pickled and then galvanised in less than one hour. No further treatment at site is anticipated for 15 years.

Structures protected by galvanising plus one coat of chlorinated rubber paint are already in existence, but not as major road bridges.

Zinc and aluminium applied as flame sprayed, metal coatings and covered by a protective paint system have been used for many years in bridge protection schemes. Recent work by the Association of Metal Sprayers has indicated that a low viscosity sealer coat (usually based on a vinyl, phenolic or polyurethane resin) may be used to seal the pores of the sprayed-metal layer and improve its durability to such an extent that further covering with paint is claimed to be unnecessary for many years.

Nylon, epoxy and PVCl powder coatings have been used for bridge parapet railings and motorway sign gantries.

The cost of protection must be a major factor in determining to what extent steel will maintain or enlarge its share of the market. Good, detailed design, together with careful selection and application of the best available materials, combined with regular and proper planned maintenance, appears to satisfy the present requirements. It is against this background that the future of the bridge painting industry will be decided.

Acknowledgments

References

The following literature is referred to in the text and recommended for further reading:

1. Ironbridge Gorge Museum Trust.
2. de'Mare, E., "Bridges of Britain".
3. "The Forth Bridge", British Rail (Scotland) publication.
4. "Forth Road Bridge", published by the Kynoch Press.
5. Transport & Road Research Laboratory Report LR. 583.

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:*

A fracture mechanics approach to lacquer cracking *by J. C. Reid*

Analysis of polyamide resins: a co-operative IUPAC study. Part II *by L. A. O'Neill and G. Christensen*

In-situ epoxidation of linseed oil in the presence of ion-exchange resins *by B. M. Badran, F. M. El-Mehelmy and N. A. Ghanem*

In addition to the above papers and regular features, the August issue will contain: the full list of past Presidents, present members of Council, Committees of Council and Section Officers and Committees; the Annual Report of the Incorporated Association for 1975 and the report of the 1976 Annual General Meeting; and lists of Section meetings for the 1976/77 session.

Review

Computer colorant formulation

By R. G. Kuehni

Farnborough, England: Lexington Books 1975

1st Edition. Pp xii + 120. Price £8.25

As the author states in the preface, this book fills a void which has existed for many years in the subject. It directs itself to colourists, systems analysts and management. In content the book brings together work which has appeared before in a wide scatter of journals throughout the world and attempts to arrange it in a logical fashion.

It begins by briefly reviewing essential aspects of colour science and turbid media theory. Not surprisingly the Kubelka-Munk analysis is the cornerstone of that which follows. The additivity function for the case of substrate only scattering—that is, dyed textiles and many scattering component systems, such as paints—are discussed with emphasis on empirical techniques to avoid problems of non-linearisation. The reader is then introduced to colourant calibration calculations and procedures.

A whole chapter is devoted to essential mathematics, the work mainly following the classic papers of E. Allen. Here will be found many of the important equations used in such programs, although the reviewer found some of the explanatory paragraphs somewhat abridged. The author deals with the two parts of a formulation program separately: the initial solution and the iterative correction. Batch correction is discussed, followed by a consideration of hiding power and the special problems introduced by fluorescence. The reader will next discover two important things: a very useful abridged flowchart of a formulation program and a step-by-step guide to the work required in order to implement a colourant formulation system. Advice is given on the different facets of such a system, including paragraphs on particular industries, and the benefits which could be expected from it. The author concludes by assessing the limitations of such formulation systems and their cause. There are 103 references.

In places, the reviewer felt that there were omissions or that the book did not go into detail; for example, there is no mention of computer storage use or program efficiency, which may be a problem when implementing Allen's "nearly empty" 16×16 matrices on a minicomputer. However, as an essential introduction it is recommended.

M. R. LUCAS

Section Proceedings

Manchester

Films—formation and behaviour

As part of its 50th anniversary celebrations, the Section held an international symposium "Films—formation and behaviour" on 6 and 7 April 1976 at the University of Manchester Institute of science and Technology. A total of 120 delegates attended the symposium, and 100 delegates were present at the symposium dinner at the Grand Hotel, Manchester, on the night of 6 April.

The Section was gratified that four of the lecturers came from within the Section area, whilst a further eight were from overseas.

The keynote address was given by Prof. Penney of Liverpool University, who took as his subject "Creativity in science and engineering and the effect of present education on this". Time and again during the discussion periods on the various papers, reference was made to Prof. Penney's contribution.

The Session Chairmen were Dr F. M. Smith, Mr H. R. Touchin, Mr C. Barker and Mr T. E. Johnson. This was a most enjoyable and instructive symposium, which rounded off the Section's anniversary year in grand style. The Section Committee takes this opportunity to thank Mr A. C. Jolly for his efforts in organising such a highly successful symposium.

It is expected that the majority of the papers will be published in due course in the *Journal.*

A.McW.

Information Received

Burrell/Cappelle Frères form new organisation

Two independent pigment producers, Burrell & Co. Ltd of London and Capelle Frères, manufacturers in France and Belgium, have formed a joint organisation, Chemie Union.

The move has been made primarily to enhance, through co-operation, joint and individual progress. Areas of particular interest will be research and development, factory processes and production methods. The companies confidently expect that significant benefits will derive from this relationship.

Under French law, the new organisation is termed "un groupement d'interest economique", a legal entity which is said to be ideally suited to joint co-operation of this nature.

Burrell, a British public company, and Cappelle Frères, a private company, are of a similar size with broadly complementary product ranges and both specialise exclusively in the chemical colour industry.

Cryogenic vessels and vacuum pumps

Boro Labs Ltd, Aldermaston, Berks has been appointed distributor for the range of cryogenic vessels manufactured by Statebourne (Cryogenics) Ltd, and distributor for the Jigtool range of vacuum pumps, which are of Australian origin and which are now manufactured in the UK.

Erlich appointed agency

G. J. Erlich Ltd, London, has been appointed sole distributor in the UK and British colonies by Expando Seal Tools of America, manufacturer of a range of maintenance tools.

As mentioned in the OCCA-28 Exhibition Preview in the March issue, G. J. Erlich has also recently been appointed UK distributor for the Copalin SA (of Greece) range of products, including ester gums, and phenolic and maleic modified resins.

F.T. Instruments—change of address

F.T. Scientific Instruments Ltd has moved to Station Industrial Estate, Bredon, Tewkesbury, Gloucestershire GL20 7HH. The company markets thermostats, densitometers, photometers and other equipment for industry and the laboratory.

"In-can" preservation

The Paint Research Association has recently commenced a multi-client programme to examine the efficiency of existing commercial non-mercurical bactericides for the in-can preservation of water-based paints and adhesives. If none of these proves adequate, the intention is to continue screen testing to discover a new non-poisonous material with the required preservative properties.

Selective growth for Shell polymers business

The Royal Dutch/Shell Group expects its polymer business (outside North America) to double from the present level of around one million tonnes a year by 1985.

This forecast was made recently by Dr J. P. Fortuin, General Manager

A general view of the Polymers Centre, Koninklijke/Shell-Laboratorium, Amsterdam
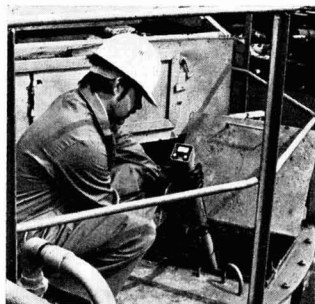
Polymers, Shell International Chemical Co. Ltd, at a meeting to mark the opening of the new Polymers Centre at the Shell laboratory complex in Amsterdam.

Shell companies have been manufacturing polymers for 30 years and the Group now has an interest in nearly 50 plants in more than a dozen countries around the world.

In the polymer industry, generally, the profit record in some areas has been below average and the Group believes that a selective approach will be necessary in the future. Shell has already withdrawn from some fields, such as general purpose rubbers in the USA and high density polyethylene in the UK, and there is the possibility of further withdrawal from other lines, which prove uneconomic.

The "Tanktector" being used to detect failures in the lining of a storage vessel (see "New products" section on page 261)

The main strengths in the Shell polymers business are in polypropylene, epoxy resins, urethane chemicals, and thermoplastic rubber. Substantial prospects for growth in these four areas are foreseen and a major drive to develop Shell's position is being made. Expandable polystyrene is also a growth area in which Shell intends to participate. Growth will not be uniform for all products. Only a modest increase is expected for general purpose rubbers, and low density polyethylene is now well established and will grow more slowly than hitherto.

The new Polymers Centre at Amsterdam brings together on one site all of the Group's R & D effort on polymers (outside North America). It will be a powerful contributor to profitability by maintaining and strengthening the necessary technical support for growth in the product areas outlined above.

Mirror backings

Batchelor Robinson Coatings Ltd, Aldridge, West Midlands, manufacturer of industrial powder coatings and paint for industry, has recently signed an exclusive UK and Ireland manufacturing agreement with Merckens Lackchemie of Eschweiler, Germany. Merckens is believed to be the largest mirror backing producer in Europe. Its products are used worldwide.

The agreement permits BR Coatings to manufacture and market under licence mirror backing throughout the UK and Ireland. This is the first time Merckens has signed such an agreement with a British company, and it will operate for an initial period of five years. New production
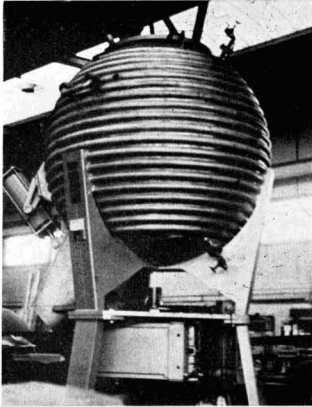
One example of the range of five spherical disperser and mixer units now being marketed in the UK by Delwin PMF Ltd, London. The units are manufactured by the SEM organisation in France and known as the "Heliglobe" range

equipment has been installed at the BR Coatings plant at Aldridge, where factory expansion is nearing completion.

Merckens mirror backing coatings are particularly suitable for roller or curtain coating applications. A full range of coating colours can be supplied to mirror manufacturers.

Literature

Adhesives directory

"Adhesives Directory 1976" has been published recently by A. S. O'Connor & Co. Ltd. The directory is now in its tenth year of publication. The current edition comprises 194 pages and a fold-out "adhesive selection" chart and costs £2.75 including 25p postage from: A. S. O'Connor & Co. Ltd, 26 Sheen Park, Richmond, Surrey.

New manuals from ECC

English China Clays (Sales) Ltd has produced three new manuals for the paint industry and a fourth is to be published in 1977. The three now available have been prepared to give the best possible treatment to the whole subject of extender usage in paint manufacture and include information about the ECC group and the many services available to its customers. The titles are: "ECC at your service"; "ECC extender pigments—characteristics and data"; and "Investigations and test methods". Copies are available from ECC's Advertising Department, John Keay House, St. Austell, Cornwall.

Plastics market

Frost & Sullivan Ltd, London, has completed a 207-page report (plus 43 pages of appendices) analysing and forecasting the market up to and including 1985 for plastics materials, by country, for products in the following categories: semi-structural buildings (eight products); furniture and soft furnishings (10 products); consumer durables and home electrics (nine products); and

housewares and "personal care" items (three products). Copies of the report are available at £300.00 each.

New products

Tanktector

Elcometer Instruments Ltd has available a new instrument, the "Tanktector", designed to detect cracks or holes in the non-conductive linings of steel tanks or vessels containing corrosive liquids.

A major feature of the instrument is that tests are undertaken whilst the contents are still in the tank. It operates without an external power source, obtaining current from the electrolytic action of the corrosive liquid into which it is placed and two integral electrodes, which form part of the instrument's body. The tanktector was developed by ICI's North and West Region Control Engineering Laboratory and is to be manufactured and marketed on a world wide basis under licence by Elcometer.

New antifouling coating

Torpedo Marine Paints, part of the Industrial Division of Berger Paints, has introduced recently a new antifouling formulation for ships' hulls called "Torflo".

The new coating is a high performance product designed to give a ship's hull a smooth surface from the moment it is applied and to offer full antifouling protection for approximately two years. The formulation is the result of a seven-year research programme and is intended to offer economies for both ships in service and new structures. For ship repainting, one coat of Torflo providing a dry film thickness 125 microns is suggested, after a sealer coat has been applied. With new buildings, a three-coat system, giving a total film thickness of 375 microns, is recommended.

The new coating is applied quickly and easily by airless spray to produce a hard, durable, corrosion resistant paint film with a uniform surface and high degree of impermeability. The new product was recently launched at a press conference given by Berger on HMS Belfast, when the technicalities of the system were explained by Mr K. Baxter, of Berger Paints and a past representative on Council for the Newcastle Section.

Conferences, symposia, etc.

South Africa—Non-conventional coatings

The sixth National Symposium of the South African Sections of the Oil and Colour Chemists' Association, sponsored and arranged by OCCA in collaboration with the South African Council for Scientific and Industrial Research (CSIR), will be held at the Holiday Inn, Summerstrand, Port Elizabeth on Friday and Saturday, 8/9 October 1976.

The theme of the symposium will be "Non-conventional coatings" and the papers to be presented will cover a wide range of topics, concentrating on the more sophisticated aspects of surface coatings technology.

Sixteen papers will be presented and a programme of social functions has been arranged. Further information may be obtained from the Symposium Secretariat, S125, CSIR, P.O. Box 395, Pretoria 0001.

New Zealand—OCCA Annual Convention

The Annual Convention of the Auckland and Wellington Sections of OCCA will be held this year from 29 July to 1 August at Rotorua on North Island. Further details can be obtained from the Honorary Secretary of the Wellington Section, Mr T. J. O'Flynn, 33 Rawhiti Street, Stokes Valley, Lower Hutt, New Zealand.
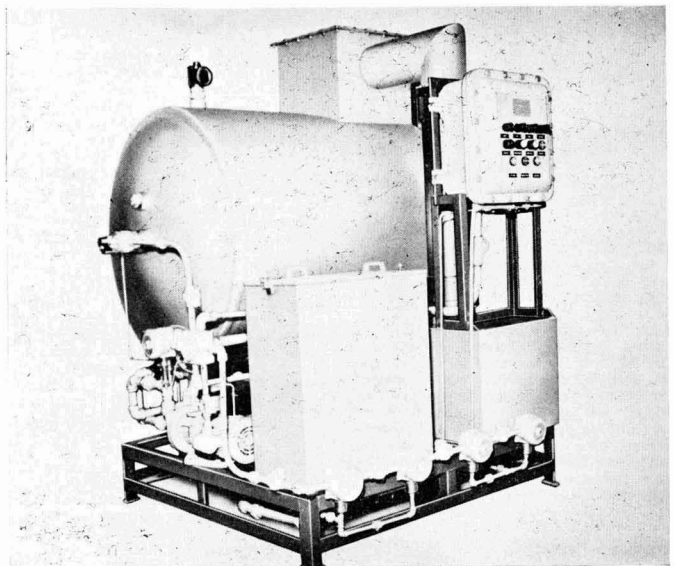
The new "Interdyne" solvent recovery system, which operates on low pressure, live steam injection; standard units are available to process at rates from 45 litres per hour upwards. Full specifications can be obtained from Planotex GmbH, Munich

OCCA-29 Exhibition

Alexandra Palace, London.   22 to 25 March 1977

The international annual
FOCAL POINT

for the

surface coatings industries

Arrangements for OCCA-29

The Exhibition Committee announces that the twenty-ninth annual exhibition of raw materials, plant and equipment for the paint, printing ink, colour and allied industries organised by the Association will take place at Alexandra Palace, London N22 from 22 to 25 March 1977. Alexandra Palace was the venue for the exhibition held in March 1976 and for the series of exhibitions from 1965 to 1969.

The Committee emphasises on this occasion the quality of the OCCA exhibitions in providing every year a focus for all those connected (either as suppliers of raw materials and equipment, or as buyers or in some other capacity) with the many and varied surface coatings markets throughout the world. The exhibition has long been known as the annual international forum for display and discussion in the surface coatings industry, and the motif for 1977 draws attention to the concept of the annual "focal point" for the industries:

Motif of the Exhibition

The motif, designed by Robert Hamblin, uses red arrows to symbolise how exhibitors and visitors are drawn from all points of the compass to the exhibition. The heads of the red arrows form white arrows in the opposite direction showing the subsequent spreading of knowledge of technical advancements from this unique annual focal point for the surface coatings industries. The colours of the motif are shown in the advertisement on the back outside cover of this issue and these colours will be carried throughout the publicity leading up to the exhibition. As the exhibition takes place at the end of March, two of the colours (green and yellow) will be incorporated on the fascias of the stands and it is intended to organise complementary floral displays of daffodils. This use of the colours will give the exhibition both an entity in its design and will afford pleasing differences in colour as visitors move from corridor to corridor, since the green colour will be used from north to south and the yellow colour from east to west.

Invitation to Exhibit

Copies of the Invitation to Exhibit have been despatched to companies and or-

ganisations in the United Kingdom and overseas which have shown at previous OCCA exhibitions or have requested information for the first time for the 1977 exhibition. Completed application forms for stand space must be returned to the Director & Secretary of the Association not later than **Friday 1 October 1976.**

The Exhibition Committee was particularly pleased to see the number of overseas companies showing at OCCA-28, either directly or through their British associates, as this emphasises the international character of the function, and any organisation in any part of the world wishing to exhibit should write immediately for details to the Director & Secretary of the Association, since exhibitors and visitors alike are welcomed from all countries.

Any organisation which has not previously exhibited and wishes to obtain an Invitation to Exhibit should contact the Association's offices immediately.

Facilities at Alexandra Palace

Visitors this year were impressed by the facilities available, which include two restaurants, two bars, a cafeteria and an exhibitors' bar. Other facilities include ample free car parking space, which is of considerable benefit especially to those using the M1 motorway, which links with the North Circular Road as shown in the map on page 268.

It will also be seen from the map that the Association will once again be organising a free bus shuttle service to and from Turnpike Lane Station on the London Underground (Piccadilly Line). The journey from central London on the Piccadilly Line takes approximately 18 minutes and connections to the Piccadilly Line can be made easily from all mainline stations. It is hoped that the new electrification of British Rail services will be completed by March 1977 so that some visitors may find it easier to travel by train from King's Cross to Wood Green Station, from which station the London Transport W3 bus travels to Alexandra Palace. A further link which will be of benefit for those travelling by air will be the extension of the Piccadilly Line to Heathrow Airport, which is scheduled for completion in 1977. This will give a direct link with Turnpike Lane Station and in the meantime a bus service operates from Heathrow Airport to Hounslow West Station. Visitors who prefer

to travel from Heathrow Airport to the West London Air Terminal in order to leave their luggage at hotels, can board the Piccadilly Line trains at Gloucester Road Station. The map will be reproduced in copies of the "Official Guide" to the exhibition which will be available in advance of the exhibition dates. The Association is able to arrange for the exhibition to be held on its own at Alexandra Palace, which means that the facilities are enclusively available for exhibitors and visitors to this important international meeting place. The Exhibition Committee, therefore, draws particular attention to this aspect of this annual exhibition in providing an annual international focal point for the surface coatings industries, where the display and discussion of technical developments and knowledge can take place in an informal atmosphere. In pursuance of this idea, the Committee has decided to amend the regulation which has previously precluded exhibitors from offering alcoholic refreshments to visitors on their stands. The Committee feels certain that the relaxation of this rule will be welcomed by exhibitors and visitors alike.

Information in foreign languages

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

"Official Guide"

This unique publication will contain descriptions of all exhibits and advertising space is available both to exhibitors and those organisations not able to show at the 1977 Exhibition. The "Official Guide" will be published **at the end of January 1977**, so that intending visitors can obtain copies and plan their itineraries.

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

As for the 1976 exhibition, copies of the "Official Guide" and season admission tickets will be available several weeks in advance of the exhibition (prepayment only) from the Association's office and they will also be available for purchase at the

entrance to the Exhibition Hall.

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

For the last two exhibitions, it was decided that a small charge should be made both for the "Official Guide" and for season admission tickets to the exhibition. This policy undoubtedly deterred casual visitors who might otherwise be attracted to exhibitions for which no admission charge was made and who gathered quantities of technical literature from the stands. The innovation was welcomed by many exhibitors and in no way acted as a deterrent to visitors to this exhibition. A similar charge will be made for the "Official Guide" to OCCA-29.

Alexandra Park and locality

There are adequate car parking facilities available at Alexandra Palace. Visitors travelling by road may consult the simplified diagram on page 268 showing the approach roads from central London and the motorways, and the enlargement above, of the area around Alexandra Park. The entrance through Dukes Avenue is for *pedestrians only*.

(*See also page 268*.)

News of Members

Mr S. Oswitch, an Ordinary Member attached to the General Overseas Section and an Associate in the Professional Grade, has recently been elected to the fellowship of the Plastics and Rubber Institute. Mr Oswitch is currently on assignment to Orlite Engineering Co. Ltd, manufacturer of plastics for Israel Aircraft Industries Ltd.

Mr J. Bowden, an Ordinary Member attached to the Scottish Section, has been appointed Technical Director of the Scottish coatings manufacturer, C-Cure Coatings Ltd of Glasgow.

Mr Bowden, an industrial chemist, has been with the parent company, P. W. Hall Ltd, in overall charge of production for the past three and a half years, and he will retain this responsibility alongside his new role. His recent promotion follows the successful introduction by C-Cure Coatings Ltd of a range of high performance "anti-graffiti" coatings for buildings.

Commendation Awards

Council approved in January 1969 the institution of a Commendation Award for outstanding and long service to the Association particularly at Section level.

Recently, Council has authorised the presentation of two more Commendation Awards, to Mr G. F. Jones of the Irish Section and to Dr W. Carr of the Manchester Section.

On 19 March 1976, Mr Jones was presented with a commemorative scroll by the Chairman of the Irish Section, Mr D. P. Power, to mark the Award. The wording on the scroll reads:

The Council of the Association has this day authorised the presentation of this COMMENDATION AWARD upon George Francis Jones in recognition of the outstanding part he has played in his constant support of Sections of the Association during his membership. During the war years he represented the Scottish Section on the Council and later served on the London Section Committee. He was a member of Council 1938-1940 and 1956-1958 and served as a Vice-President 1959-1961. On moving to the Irish Section in 1967 he has at all times rendered support and assistance to the Section, serving for several years as Training officer.

It is signed by the President and Honorary Secretary of the Association, the Chairman of the Irish Section and the Director & Secretary.

Dr Carr also received an Award this year. The scroll was presented to him on 6 April 1976 by the Chairman of the Manchester Section, Mr H. G. Clayton, and reads as follows:

The Council of the Association has this day authorised the presentation of this COMMENDATION AWARD upon William Carr, Doctor of Philosophy, Fellow of the Association in the Technology of Surface Coatings, in recognition of his outstanding contribution to the Association by his lectures presented to the Association's Conferences, Sections and Branches, both in the United Kingdom and abroad; his representation of the Association through the presentation of papers to sister societies overseas, and the outstanding number of communications written by him for the Association's Journal over a period of 30 years.

It is signed by the President and Honorary Secretary of the Association, the Chairman of the Manchester Section and the Director & Secretary.

A full list of those Members who have received a Commendation Award will be published in the August issue of the *Journal*.

Mr G. F. Jones (right) receiving his Commendation Award from the Chairman of the Irish Section, Mr D. P. Power

Dr W. Carr with his Commendation Award

Association Conference 1977

The next biennial conference of the Association will be held at the Grand Hotel, Eastbourne, from Thursday 16 to Sunday 19 June 1977 and the theme for the conference will be:

The conservation of energy, materials and other resources in the surface coatings industry

It is intended that as on previous occasions, full preprints will be published for despatch to delegates in advance of the Conference. It is important, therefore, that any person, whether or not a Member of the Association, who feels that a report of his work could form the basis of a suitable

paper should contact immediately the Honorary Research and Development Officer by writing in the first instance to the Director & Secretary of the Association at the address on the Contents page of this issue.

It will be recalled that it is the custom at the Association's Conferences for the authors merely to outline their papers, highlighting points of interest, and for a general discussion of the paper to follow. The author will not be expected to deliver the paper *in toto*, since the object of sending out the preprints in advance is that delegates may read these thoroughly before the Conference.

Optional Professional Grade for Ordinary Members

The innovation of the Professional Grade has proved to be most successful, as evidenced by the impressive list of names in the December 1975 issue of the *Journal*. For the convenience of potential applicants, a chart indicating different routes to the various grades is shown below.

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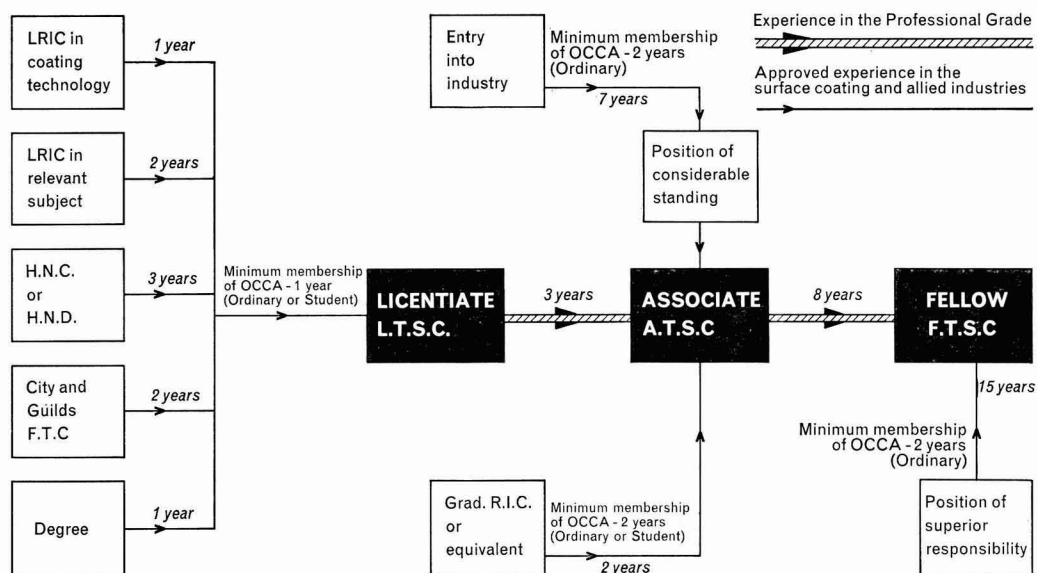
Note: At present there is no restriction on Students up to 21; between 21 and 25 a certificate from the employer or college confirming the course being taken is required.

Regulations for admission to the Professional Grade

Note: For the sake of simplicity, reference is made only to UK examinations etc., but equivalent qualifications overseas will naturally be accepted.

A. Licentiate

1. Shall be an Ordinary Member of the Association and have been an Ordinary Member or Student of the Association for not less than one year.

2. Shall have attained the age of 22.

3. (a) Shall be a Licentiate of the Royal Institute of Chemistry in Coatings Technology (*viz.* Higher National Certificate + Endorsement in coatings technology + 1 year approved experience in the science or technology of coatings after passing the endorsement examination).

OR (b) Shall be a Licentiate of the Royal Institute of Chemistry in another relevant subject such as advanced analytical chemistry, colour chemistry or polymer science, and shall have two years' approved experience of coatings since so qualifying.

OR (c) Shall hold the Full Technological Certificate of the City and Guilds of London Institute in a relevant subject as approved by the Professional Grade Committee and shall have two years' approved experience in the science or technology of coatings since gaining the FTC.

OR (d) Shall have passed Higher National Certificate or Higher National Diploma with three years' approved experience in the science or technology of coatings since qualifying, but two years' approved pre-qualification experience shall be deemed equivalent to the third post-qualification year.

OR (e) Shall be graduate in relevant subject with not less than 1 year's approved experience.

OR (f) Shall have passed such other qualifications as approved by the Professional Grade Committee from time to time.

4. Shall be required to satisfy the Professional Grade Committee, or some other body approved by the Professional Grade Committee in a *viva voce* examination and submit a dissertation on a topic previously approved by the Professional Grade Committee.

5. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade (either Associate or Fellow) at least one of whom must be a Fellow.

6. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

B. Associate, being already a Licentiate

1. Shall, since his election to the Licentiate-ship, have practised the science or technology of coatings for not less than three years.

2. Shall provide evidence acceptable to the Professional Grade Committee of his superior professional skill and maturity.

3. Shall hold the City & Guilds of London Institute Insignia Award OR shall submit a thesis or dissertation of comparable level on a topic previously approved by the Professional Grade Committee OR shall have published work which, in the opinion of the Professional Grade Committee, is of comparable merit.

4. MAY be required to satisfy the Professional Grade Committee or some other body as approved by the Professional Grade Committee in a *viva voce* examination.

5. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade (either Associate or Fellow) at least one of whom must be a Fellow.

6. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

C. Associate, not already a Licentiate

EITHER

1. Shall be not less than 24 years of age.

2. Shall be an Ordinary Member of the Association and have been an Ordinary Member or Student of the Association for not less than two years.

3. Shall hold the Graduateship of the Royal Institute of Chemistry or Council of Physics or a University or Council of National Academic Awards degree recognised by the Royal Institute of Chemistry or Institute of Physics as giving full exemption from the Graduateship examination.

4. Shall have not less than two years' approved post-graduate experience in the science or technology of coatings.

5. Shall normally be required to satisfy the Professional Grade Committee or some other body approved by the Professional Grade Committee, at a *viva voce* examination.

6. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade (either Associate or Fellow) at least one of whom must be a Fellow.

7. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

OR

8. Shall be not less than 30 years of age.

9. Shall be an Ordinary Member of the Association and have been an Ordinary Member of the Association for not less than two years.

10. Shall have been engaged in practising the science or technology of coatings for not less than seven years and shall have attained a position of considerable standing in the industry.

11. Shall normally be required to satisfy the Professional Grade Committee in *viva voce* examination of his professional competence.

12. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade (either Associate or Fellow) at least one of whom must be a Fellow.

13. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

D. Fellow

Note: This is the senior award of the professional grade and signifies that the holder has made outstanding contributions to the science or technology of coatings or has reached a position of eminence in the industry through the practice thereof. The Professional Grade Committee will require substantial evidence of professional maturity in the science or technology of coatings although commercial experience will be taken into account in assessing the merits of candidates.

1. Shall be not less than 33 years of age.

2. Shall have been an Ordinary Member of the Association for not less than two years.

3. Shall be engaged in a position of superior responsibility in the coatings industry.

4. EITHER (a) shall have been an Associate of the professional grade for at least eight years;

   OR   (b) shall have not less than fifteen years' experience of the science or technology of coatings in a position of superior reponsibility.

5. Shall submit, with his application, an account of his experience, with due reference to scientific and technological interests, achievements and publications.

6. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade, all of whom must be Fellows.

7. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

The fees payable with applications are as fellows:

Fellow—£10.00   Associate—£6.00
Licentiate—£3.00
(Plus VAT at standard rate)

Application

Completed application forms should be returned, together with the appropriate remittance, to the Director & Secretary at the Association's offices (except in the case of those Members attached to the Auckland, South African and Wellington Sections who should address their forms to their Section Hon. Secretaries).

The Committee wishes it to be known that Members rejoining the Association after a period in other industries may include length of service as an Ordinary Member before their resignation as part of the qualifying periods for entry into the Grade.

Students wishing to apply for entry into the Professional Grade must first make application in writing for upgrading to Ordinary Membership, giving the reasons for their eligibility for such regrading. Applications, together with the appropriate remittance, should be addressed as for application for admission to the Professional Grade.

Potential applicants are recommended to give the fullest possible details of their appointments, including the number and type of staff under their control, and indicating to whom the applicant is responsible, as this aids the committee considerably in its deliberations.

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

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

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

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

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

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

Length: Text should be approximately 5 000 words.

Applicants should refer to the paper by Moss which appeared in the January 1973 issue; the Professional Grade Committee feels that candidates for the Licentiate grade could with advantage use this paper as a model for their dissertations.

Association Dinner and Dance 1976

The Association's biennial Dinner and Dance was held this year on Friday 14 May at the Savoy Hotel, London, when approximately 230 members and guests were received by the President, Mr A. T. S. Rudram and Mrs Rudram.

After dinner, the President first proposed the loyal toast and then welcomed the Association's guests and ladies. The principal guests were as follows:

Mr R. T. Bowes (President of the Society of British Printing Ink Manufacturers) and Mrs Bowes.

Mr F. J. Briggs (Chairman of the Research Association for the Paper and Board, Printing and Packaging Industries) and Mrs Briggs.

Mr G. K. Burrell (Chairman of the British Colour Makers' Association) and Mrs Burrell.

Mr I. Gailey (President of the Society of Dyers & Colourists) and Mrs Gailey.

Mr A. G. Ingram (Master of the Worshipful Company of Painter-Stainers) and Mrs Ingram.

Professor J. S. Llewelyn Leach (President of the Institution of Corrosion Science & Technology) and Mrs Llewelyn Leach.

Mr H. Rose (President of the Paintmakers' Association of Great Britain Ltd) and Mrs Rose.

Dr F. M. Smith (President of the Paint Research Association) and Mrs Smith.

The Association's Guest of Honour on this occasion was Dr J. Edwards (President of the Institute of Metal Finishing), accompanied by Mrs Edwards and Mr Rudram reminded those present that this year the IMF was celebrating its fiftieth anniversary. He looked forward to many more years of goodwill and co-operation between the Association and the Institute.

Dr Edwards replied to the Address of Welcome by the President, after which dancing to the Jerome Orchestra continued until the early hours.

Photographed at the Association's 1976 Dinner and Dance (from left to right): Dr J. Edwards (President of the Institute of Metal Finishing and principal guest), Mrs Edwards, Mrs Rudram, and the President, Mr A. T. S. Rudram

London Section

Annual General Meeting

The Annual General Meeting of the Section was held at the Piccadilly Hotel, London W1, on Thursday 22 April 1976.

The annual Kekwick Prizes were given to students of London colleges, who had shown outstanding ability and who were taking courses or had completed studies in surface coatings technology. The list of those who received the awards has been published in the *Journal* (see page 154 of the April 1976 issue).

Mr I. W. Hardie and Miss J. Matthews receive their Kekwick Prizes from Dr Kekwick. Also shown in the photograph are Mr Worsdall (seated) and Mr Tooke-Kirby (extreme right)

The Section Officers and Committee were elected for the 1976/77 session and these will be published as usual in the August issue.

Mr H. C. Worsdall was presented with a silver cream jug in recognition of his work as Honorary Secretary, and he was elected Honorary Symposium Secretary. Acknowledgment was also given to the excellent work which had been done by Mr B. A. Canterford,

despite physical disabilities, during his term as Honorary Publications Secretary. Mr J. Tooke-Kirby was re-elected Chairman and he paid tribute to the support he had received from the Officers and Committee.

Mr Worsdall was charged with the duty of presenting a suitably inscribed gavel and block to the newly constituted Ontario Section at its AGM (see page 267).

The number of Members and ladies present was approximately 40, and included several past-Chairmen and Officers of the Section (amongst whom it was noted with pleasure were the President and Mrs Rudram). A buffet meal was served after the AGM, and this was followed by a most interesting talk by Dr R. J. Ceresa on "The restoration of a Tudor house," illustrated by slides, which greatly contributed to the success of the evening.

Mr J. Tooke-Kirby, Chairman of the London Section, presents a silver cream jug to Mr H. C. Worsdall (left) in recognition of his services as Honorary Secretary of the London Section

Ontario Section

Annual General Meeting

The Ontario Branch of the London Section was formed in May 1975, as reported in the July 1975 issue of the Journal. *So rapid has been the progress and growth of the Branch that it was accorded Section status at the April 1976 meeting of Council. The change-over from Branch to Section status was to take effect from the date of the first Branch AGM, and a report of that meeting appears below.*

The first Annual General Meeting of the Ontario Section was held at 7.00 pm on 28 April 1976 at the Skyline Hotel, Toronto, with Mr P. Birrell in the chair. Only 12 months after the first Annual General Meeting of the Ontario Branch, the presence of 39 Members was encouraging. The chairman recalled the first meeting, when no funds at all existed and when the meeting had been held in a public lounge.

The AGM was preceded by a reception and dinner, during which the Honorary Secretary and past Chairman of the London Section,

The Committee of the new Ontario Section with Mr H. C. Worsdall, who will be the Section's representative on Council

Mr Birrell then announced that following the authorisation by OCCA Council in their minute 34 of the meeting of 24 February 1976 the Ontario Branch had attained the status of a Section of OCCA. Mr Worsdall said he was delighted to have the pleasure of presenting the Insignia of Office. He felt the honour was well deserved by Mr Birrell, who had had experience in the Scottish Section as vice-chairman and had assisted in the education of the junior Members, and he felt the Section was in capable hands. The fact that the "spearhead" of the Section was the technical education of ink technologists, was perhaps an omen for the future. Mr Worsdall went on to say that a first-class Chairman appeared to have a first-class Committee and what was more, a Committee on which youth was represented. He ended by conveying the best wishes of Council and the London Section Committee.

There was no further business, and Members were able to enjoy the social side of the meeting for the remainder of the evening.

Mr Worsdall was elected at the Committee meeting to represent the Ontario Section on Council. He will be pleased to answer queries in the UK.

Mr P. Birrell (left), Chairman of the Ontario Section, receives a gavel and block from Mr H. C. Worsdall (then Honorary Secretary of the London Section) on behalf of the London Section

Mr H. C. Worsdall was introduced to the newer Members. Mr Worsdall brought good wishes and congratulations from the UK and presented Mr Birrell with an inscribed gavel and block from the London Section, and an OCCA wall plaque from himself. He said he was delighted with the progress the Branch had made since his initial meeting with prospective Members in October 1974.

At the conclusion of the dinner, the Chairman called the meeting to order; apologies were read and the minutes of the 1975 AGM, having been circulated, were adopted and signed by the chairman. The Hon. Treasurer, Mr W. Fibiger, read the financial report, which he stated would be audited after the appointment of an auditor. He explained the changes in membership and financial procedures resulting from the change from Branch to Section status. Since there were no nominations additional to those required, the meeting was asked to accept the slate of officers *en bloc*. The full list of officers and Committee so elected will be published in the August issue of the *Journal*.

West Riding Section

Luncheon Lecture

The eleventh Luncheon Lecture of the Section was held at the Astoria Ballroom Restaurant, Leeds, on 21 May 1976.

The guest speaker on this occasion was Mr R. C. Brown, Senior Industrial Relations Officer of the Advisory, Conciliation and Arbitration Service (ACAS). Mr Brown explained that ACAS was established by the Government as an independent body to provide help and advice to industry in the whole sphere of industrial relations and to conciliate in disputes should this be necessary. He pointed out that governmental involvement in industrial relations was nothing new and could be traced back to the fifteenth century. Current legislation had been influenced by, and was required upon Britain's entry into the EEC.

Mr Brown outlined the range of services offered by ACAS and discussed some typical examples of the work it performed. Several members of the audience acknowledged the help provided to their own organisations by ACAS, and a vote of thanks was proposed by Mr M. J. Cochrane.

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

AITKEN, IAN WILLIAM, BSc, 103 Chartwell, 37 Ridge Road, Durban, South Africa   (*Natal*)

BROWN, JOE, 9 Grasscroft Road, Stalybridge, Cheshire
                                                                    (*Manchester*)

FREEMAN, DENNIS BRIAN, BSc, Pyrene Chemical Services Ltd, Ridgeway, Iver, Bucks SL0 9JJ   (*London*)

HARWOOD, JAMES, BSc, 7 Cane End, Princes Risborough, Aylesbury, Bucks   (*Thames Valley*)

HODSDON, PETER JAMES, BSc, 150A Manning Road, Glenwood, Durban, South Africa   (*Natal*)

INNES, NORMAN DOUGLAS, Union Carbide SA (Pty) Ltd, PO Box 1880, Durban, South Africa   (*Natal*)
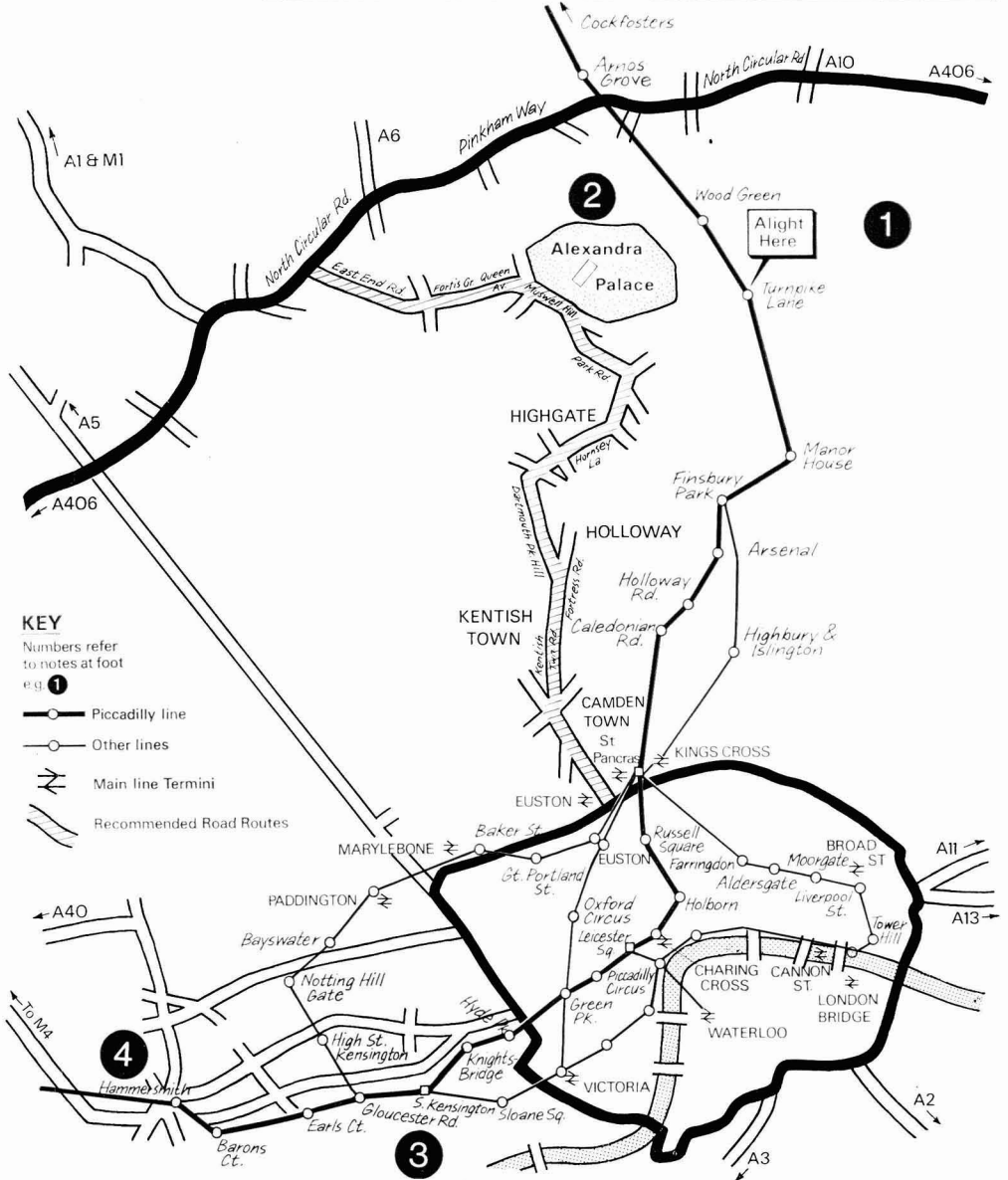
JOHNSTON, ROY AMBLER, British Industrial Plastics SA (Pty) Ltd, Box 12, Pinetown 3600   (*Natal*)

REYNOLDS, FLYNN, BSc, PO Box 22109, Glenashley 4022, South Africa   (*Natal*)

TO, LEVI, BSc, Mei Fu Sun Chuen, Stage II, 34D Broadway Street 9/F, Kowloon, Hong Kong   (*General Overseas*)

WHISTON, CHRISTOPHER JOHN CHARLES, BSc, Ciba-Geigy UK Ltd, 776 High Road, Tottenham, London N17 OBZ   (*London*)

Associate Members

GALATIS, JOHN, PO Box 948, Durban, South Africa.   (*Natal*)

GOOSEN, PETRUS JACOBUS, PO Box 280, Durban 4000, South Africa   (*Natal*)

TAYLOR, IAN, 1012 The Gables, Espeanade, Durban, South Africa   (*Natal*)

OCCA-29

For the benefit of intending visitors to the Exhibition, a map is reproduced below of the area around Alexandra Palace showing the mainline stations in central London, the Piccadilly, Circle and Victoria Lines of the underground system and also the road links with the North Circular Road and motorways. See also the enlarged map of Alexandra Palace, reproduced on page 263.

KEY

Numbers refer
to notes at foot
e.g. **1**

━━● Piccadilly line

──○── Other lines

Main line Termini

Recommended Road Routes

1. A free bus shuttle service will operate between Alexandra Palace and Turnpike Lane station on the Piccadilly Line (Underground), which is denoted by the thick coloured line. Destinations of trains may be marked as "Cockfosters" or "Arnos Grove" or "Wood Green"

2. Those travelling by road will find free car parking facilities at Alexandra Palace. See map on page 263.

3. Visitors arriving at West London Air Terminal may board the Piccadilly Line trains at Gloucester Road station.

4. At present the Piccadilly Line reaches westward as far as Hatton Cross Station and in 1977 will be extended by the addition of a further station in Heathrow Airport Terminal, so that visitors will then be able to travel direct from the airport terminal to Turnpike Lane station. In the meantime, a bus service operates between the air terminal and Hounslow West station on the Piccadilly Line.

5. The map also shows the position of the mainline stations in relation to the Piccadilly Line.

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AUSTRALIAN CORROSION CONTROL COMPANY

PROTECTIVE COATINGS DIVISION

Senior Sales Engineer

(Marine & Offshore)

The company has been operating for over 30 years and is a market leader with world-wide affiliations. It is active throughout Australasia and South East Asia, and in addition to the marine field, is involved in major projects throughout the region.

The position involves responsibility for technical sales to the Manager, Marine & Offshore, and interstate travel will be necessary in this post.

The man required will be between the ages of 28-35 years with a good general education. He will have a proven technical sales record and a background of a Coatings Technician/Corrosion Engineer or similar with considerable field exposure.

A manner and presentation which insures acceptability at all levels is imperative and evidence of a sound understanding of business fundamentals important. The man will be seeking a career appointment and will be keen to advance his standing in the company.

An attractive salary will be offered, a company vehicle and superannuation scheme apply to the appointment.

Assistance with relocation expenses will be provided.

Applications in the first instance to:

The General Manager,

F and T Dimet Marine Coatings,

P.O. Box 85,

Preston,

Victoria,

Australia 3072.

E. WOOD/COPON INTERNATIONAL

require

a senior representative qualified by experience and success in sales of anti-corrosion and chemical resistant surface coatings.

A wide circle of contacts in this market with the ability to secure new business and develop existing accounts is required combined with a basic technical understanding of the products involved.

This is an expanding and important division to which full company support is given and which offers great opportunities.

Based in the London area the right man will be paid a good salary and provided with a company car, four weeks' holiday, bonus and other benefits.

Apply with fullest personal details to:

Mr K. S. J. Fraser,
Managing Director,
E. Wood Limited,
Talbot Works,
Stanstead Abbotts,
Ware, Herts, SG12 8DP.

SITUATIONS WANTED

MISCELLANEOUS

Paint Technologist. German, aged 32, married, no children, wide experience in development and formulation of industrial paints, coatings and printing inks, seeks opportunity overseas. (Box No. 426)

INDUSTRIAL COURSE IN ELECTROSTATIC COATINGS
(Powders and Paints)

15-17 September 1976

Lectures covering both practical industrial procedures and the fundamental principles of the process will be presented.

Contact:

Dr A. Cetronio,
Department of Electrical Engineering,
University of Southampton,
Southampton, SO9 5NH
Telephone: (0703) 552266

Qualified Paint Chemist with experience in formulation, production and raw material buying seeks change from present position. Willing to work abroad where English, Spanish or Portuguese spoken. Please reply to Box No. 425 before 31 October.

Send your Classified Advertisements for JOCCA by telex on 922670 (OCCA Wembley)

Ultraviolet polymerisation and the surface coatings industry

Twelve papers with the above theme, first presented to a Symposium of the Newcastle Section in 1974 and later published in the *Journal*, are now being collated and bound into a special volume to form a comprehensive "state of the art" review of this field.

Copies, price £5.00 (including postage by surface mail) will be available shortly (prepayment only) from the Association's offices at the address on the contents page of this issue.

CLASSIFIED ADVERTISEMENTS

SITUATIONS VACANT

GEORGE M. WHILEY LTD

Leading manufacturers of hot press stamping foils, require for their new plant at Livingston, West Lothian, Scotland

Colour Matching Laboratory Assistant

SURFACE COATING TECHNOLOGIST with colour matching and ink/paint formulation experience required for the Research and Development Laboratory. Applicants should preferably be qualified to H.N.C. or equivalent. Preferred age 25/30.

The successful candidate would be required to undergo a short period of training at our Croydon, Surrey plant prior to the commencement of duties in Livingston.

Applications in writing, giving full career details, in first instance to:

Mr. N. Dollar, Personnel Manager
GEORGE M. WHILEY LTD.
Firth Road, Houston Industrial Estate, Livingston.

CHEMIST

Worldwide manufacturer of architectural coatings requires experienced chemist for its small UK subsidiary, to take charge of all research, formulating, quality control of its surface coatings. Salary open. Replies in strict confidence. Send resumé to:

Managing Director,
Kenitex Chemicals (UK) Ltd,
Amberley Way,
Hounslow,
Middlesex TW4 6BH

LABORATORY MANAGER
SWEDEN

Farg AB International is a thriving Swedish paint manufacturer part of the International Paint Group. Employing 450 people with a turnover of £18m, the company develops, produces and markets a wide range of coatings for both industry and shipping.

Due to current expansion, there is a need in the industrial finishes division for a well-qualified paint chemist who, as Laboratory Manager, will be responsible for coil coating, metal decorative and general industrial coatings.

The position involves both formulating and customer service duties and the international contacts within the IPC Group form an important and stimulating part of the work.

This is a permanent post, based in Gothenburg, and whilst a fluency in Swedish would be desirable it is not considered necessary. Salary will be very attractive, coupled with a first-class fringe benefit package, and you will enjoy a healthy standard of living in a country renowned for its beauty.

Please write giving full details to:
D. C. Powell, Group Personnel Manager,
THE INTERNATIONAL PAINT COMPANY
Henrietta House, 9 Henrietta Place,
London W1A 1AD

Association Conference 1977
CALL FOR PAPERS
See page 263

NEW OCCA TIE

Members are reminded that in addition to the original tie with a blue background, the Association now offers an alternative maroon tie with a single gold motif.

The maroon ties cost £1.85 each, including Value Added Tax, packing and postage by surface mail, and may be obtained (prepayment only) by sending the necessary remittance to the Association's offices at the address on the contents page of this issue, quoting Section, Membership number, and full postal address.

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SITUATIONS VACANT

JUBILEE DINNER (19.00 for 19.30 hours)

SESSION II	PROTECTION – Technology & Economics
Wednesday, September 22 1976. (09.15 – 12.45)	
Chairman: Mr. R. M. Woodhouse, Managing Director, International Paint Co. Ltd.	
Paper 6: Buildings	Mr. R.T. Kelly – Scientific Adviser Greater London Council
Paper 7: Marine (including offshore oil rigs)	Mr. J. Jackson – Anti-Corrosion Consultant Shell International Marine Ltd.
Paper 8: Bridges & Structures	Mr. A. Watson – Product Manager Berger Paints (Protecton Division)
Paper 9: Transport	Mr. W.F. Dabbs – Staff Director, Forward Facilities Planning, British Leyland UK Ltd.

SESSION IV	THE NEXT 50 YEARS
Thursday, September 23 1976. (09.15 – 12.45)	
Chairman: Mr. R. Chester, Chairman, Donald Macpherson & Co. Ltd.	
Paper 14: Raw Materials & the Future	Mr. G. Willison – Technical Sales Manager BTP Tioxide Ltd.
Paper 15: North Sea Oil & Chemical Based Industries	Dr. D.G. Jones – Director Corporate Laboratory, I.C.I. Ltd.
Paper 16: European Network on Information & Documentation	Mr. J.C. Gray – Director British Library, R. & D. Dept.
Paper 17: Is This the End of the Road for Research?	Dr. G. de W. Anderson – Director Paint Research Association

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