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# JOURNAL OF THE IL & COLOUR CHEMISTS' ASSOCIATION

Photoinitiation by aromatic carbonyl compounds

*A. Ledwith*

The technological literature relating to polymerisation photoinitiators

*A. Pryce*

Photopolymerisation: the kinetics of a-type photopolymerisation

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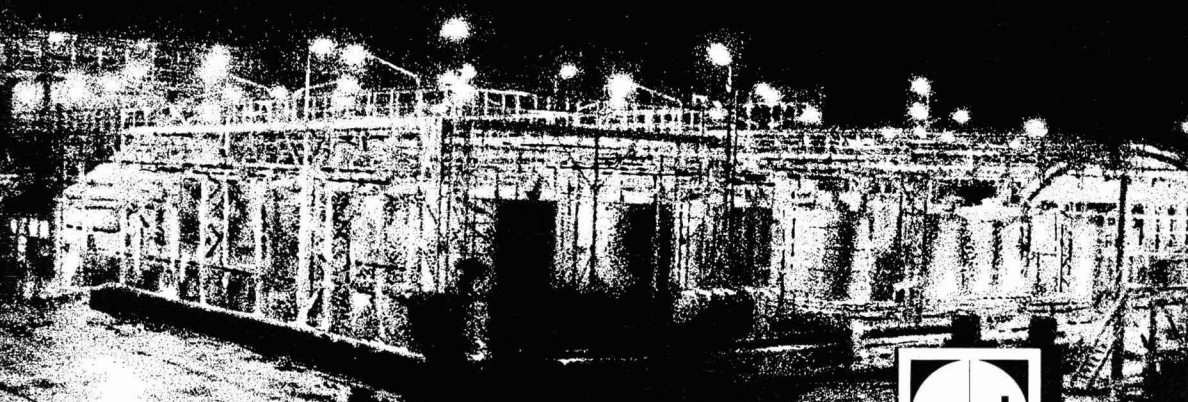
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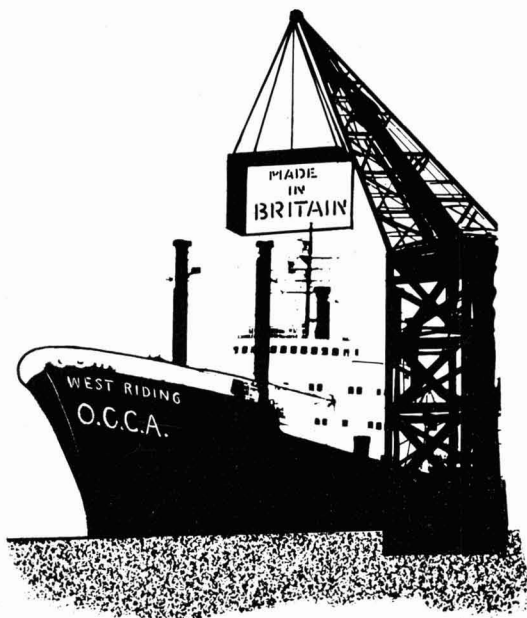


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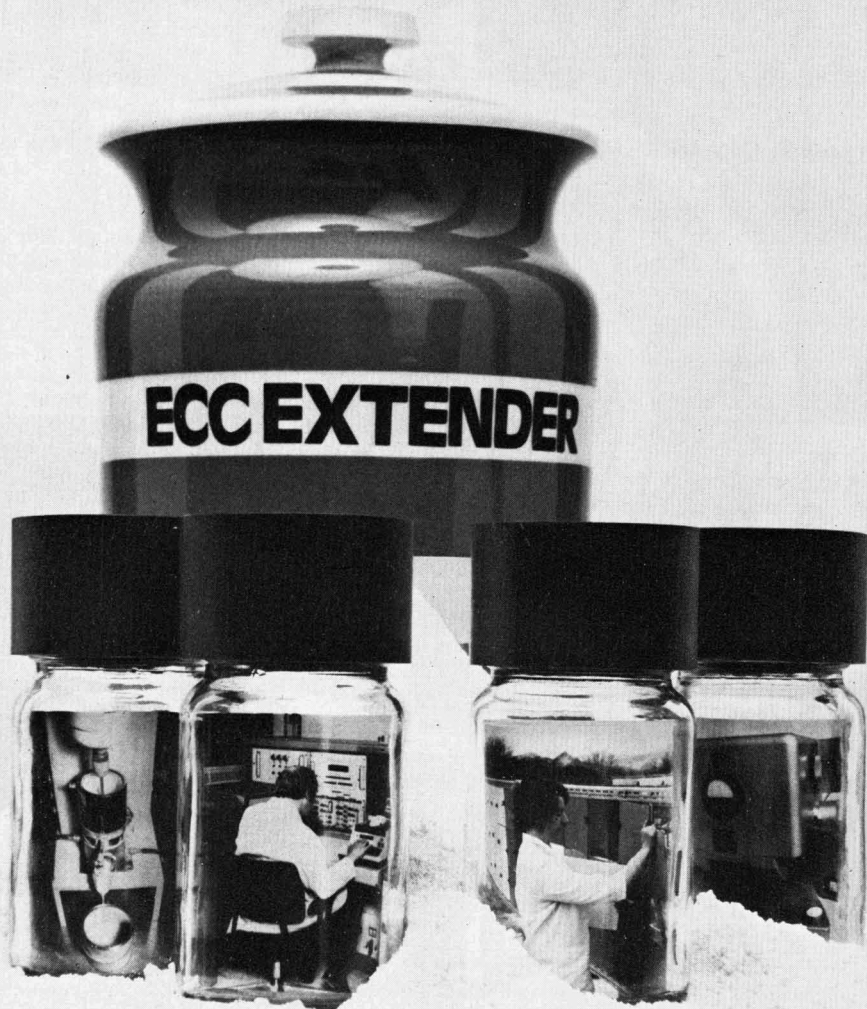
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Contents

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C

*Transactions and Communications*

**Photoinitiation by aromatic carbonyl compounds** . . . . . 157  
*A. Ledwith*

**The technological literature relating to polymerisation photoinitiators** . . . . . 166  
*A. Pryce*

**Photopolymerisation: the kinetics of a-type photopolymerisation** . . . . . 171  
*F. C. de Schryver and N. Boens*

*Section Proceedings* . . . . . 177

*Reviews* . . . . . 179

*Information Received* . . . . . 180

*Notes and News* . . . . . 183

**OCCA-28 Exhibition Review** . . . . . 183

*Register of Members* . . . . . 192

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# Photoinitiation by aromatic carbonyl compounds\*

By A. Ledwith

Donnan Laboratories, University of Liverpool, Liverpool L69 3BX

## Summary

The role of aromatic carbonyl compounds, including quinones, as active components of photoinitiating systems is reviewed. According to the nature of substituents and added substrates, photo-induced formation of free radicals may occur by homolytic fragmentation,

hydrogen atom transfer, and electron transfer processes. Applications and complications arising from the various mechanistic pathways are outlined, and the apparent activity of Michler's ketone in forming "encounter complexes" (exciplexes) is discussed.

## Keywords

Processes and methods primarily associated with:

manufacturing or synthesis  
photoinitiation

drying or curing of coatings  
photoinitiation  
photopolymerisation  
ultraviolet curing

## Photoinitiation par les composés aromatiques portant un groupe carbonyle

### Résumé

On passe en revue le rôle des composés aromatiques portant un groupe carbonyle, y compris les quinones, en tant que constituants actifs des systèmes de photoinitiateurs. A mesure de la nature des substituants et des supports utilisés, la formation de radicaux libres photoamorcés peut être produite par les processus de

fragmentation homolytique, du transfert d'ions d'hydrogène ou d'électrons. On donne une esquisse des applications et des complications qui surviennent des diverses possibilités mécanistiques et l'on discute l'activité apparente de la cétone de Michler au cours de la formation des "complexes de rencontre" (exciplexes).

## Photoinitiation durch aromatische Carbonylverbindungen

### Zusammenfassung

Eine Betrachtung über aromatische Carbonylverbindungen, einschliesslich Quinone, als aktive Komponenten von Photoinitiationssystemen. Je nach Art des Substituents und zugesetzter Substrate kann durch homolytische Fragmentierung, Wasserstoffatomübertragung und Elektronen übertragungsprozesse photoinduzierte Bildung

freier Radikale vorkommen. Sich aus den verschiedenen mechanistischen Wegen ergebende Applikationen und Komplikationen werden skizziert, und die scheinbare Aktivität von Michlers Keton bei der Bildung von "Begegnungskomplexen" (encounter complexes (exciplexes)) wird besprochen.

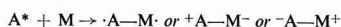
## Introduction

Refs. 1, 2

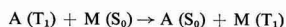
Aromatic carbonyl compounds may, under appropriate circumstances, function as photosensitisers or photochemically active initiators for free radical vinyl polymerisation. There are many reported examples of technological applications of photoinitiated vinyl polymerisations in which these compounds are active ingredients, although in many cases details of the photo-induced processes and the nature of the actual initiating radical fragments are not known. Such processes are important in the development of photochemical curing techniques for the manufacture of printed circuits, relief printing plates, and the more recent development of 100 per cent reactive systems in the coatings and printing ink industries.

In principle, there are at least five distinct mechanisms by which a photo-excited molecule ( $A^*$ ) may initiate polymerisation:

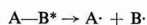
- (a) Direct addition of  $A^*$  to monomer (M) or other reaction components, producing a bi-radical or dipolar species, for example:



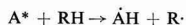
- (b) Energy transfer from (mainly) triplet excited molecules to monomer or other reaction components to produce triplet excited monomer, for example:



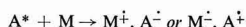
- (c) Homolytic fragmentation of the photo-excited molecule, for example:



- (d) Hydrogen abstraction by  $A^*$  from monomer or other reaction components, to produce two radicals, for example:



- (e) Electron transfer between photo-excited molecule and monomer or other reaction components, to produce a pair of ion radicals, for example:



Mechanisms (a) and (b), as written, yield mainly bi-radical intermediates which, because of facile cyclisation, are inefficient initiating and propagating species in polymerisation:

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

these processes will not, therefore, be considered further. In contrast, mechanisms (c), (d), and (e) may all be used conveniently to initiate (mainly) free radical polymerisation and it will be the purpose of this review to survey the general applicability of these processes in so far as they involve aromatic carbonyl compounds. It should be noted, however, that triplet states will be important intermediates along the reaction pathways, which lead ultimately to the reactions under (c)-(e), and bi-radicals may be important where rapid conversion to a mono-radical derivative is an available reaction pathway.

More complete accounts of the reaction mechanisms involved in photocatalysed and photoinitiated reactions of olefins involving aromatic carbonyl compounds have been given by Hutchison and Ledwith<sup>1</sup> and by Heine, Rosenkranz and Rudolph<sup>2</sup>.

### The nature and reactivity of excited states of aromatic carbonyl compounds

Molecules containing hetero-atoms have electrons in orbitals associated with the hetero-atom, which are not involved in the bonding system of the molecule. Carbonyl compounds provide good examples, since there are two electrons in each of the non-bonding ( $n$ -orbitals) of the oxygen atom. Absorption of radiation can lead to the promotion of one of these electrons into either a  $\sigma^*$  or a  $\pi^*$  orbital, that is  $n \rightarrow \sigma^*$  or  $n \rightarrow \pi^*$  transitions (Fig. 1).

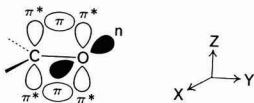


Fig. 1. Orbitals associated with a C=O group

Only one of the  $n$  orbitals is shown (represented as a  $2p$  orbital) pointing along the X-axis, whilst the  $\pi$  and  $\pi^*$  orbitals lie in the Y-Z plane

For most molecules, the energies of the various bonding and antibonding orbitals increase in the order  $\sigma < \pi < n < \pi^* < \sigma^*$  and this means that the most readily observable electronic transitions are  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  in nature. Usually  $n \rightarrow \pi^*$  transitions are lower in energy than the corresponding  $\pi \rightarrow \pi^*$  transitions, but the positions may be reversed according to the degree and type of substitution. Furthermore, it does not follow that because the lowest energy transition is usually  $n \rightarrow \pi^*$  in character, the lowest energy triplet state should be so defined.

Quite apart from relative energy levels, there are very important differences in the electronic structures and chemical reactivities of ( $n, \pi^*$ ) and ( $\pi, \pi^*$ ) excited states. Inspection of the diagrammatic representation of the orbitals of a carbonyl group, shown above, indicates that promotion of an electron from an  $n$  orbital to a  $\pi^*$  antibonding orbital has the effect of removing electron density from the oxygen atom, with the result that ( $n, \pi^*$ ) excited states (especially triplet states) display reactivity similar to that of alkoxy radicals. In particular, reactions involving hydrogen abstraction—well characterised for alkoxy radicals—are frequently encountered for ( $n, \pi^*$ ) excited states. On the other hand, promotion of a  $\pi$ -bonding electron to a  $\pi^*$ -antibonding orbital has the effect of increasing electron density at the oxygen atom, with a consequential increase in the polar nature of the  $>C=O$  group. The differing electron distributions of ( $n, \pi^*$ ) and ( $\pi, \pi^*$ ) excited states are

manifested in the effects of solvent polarities on the energies of the transitions. Increasing solvent polarity causes a decrease in the energy of  $\pi \rightarrow \pi^*$  transitions (red shift) largely because polar solvents will reduce the energy of the (more polar) excited state by increased solvation. Corresponding  $n \rightarrow \pi^*$  transitions are shifted to shorter wavelengths (higher energies) by increasing solvent polarity, and especially so by hydrogen-bonding solvents. This so-called "blue shift" results from the decrease in energy of the  $n$  orbital, consequent on hydrogen bonding or other dipolar interactions. It should be noted that some aromatic carbonyl compounds (for example, acetophenone and xanthone) have comparatively small energy separations between highest energy  $n$  and  $\pi$ -bonding orbitals and hence may give rise to the lowest ( $n, \pi^*$ ) or ( $\pi, \pi^*$ ) excited states, depending on the particular solvation environment.

Undoubtedly, the most important distinction between the ( $n, \pi^*$ ) and ( $\pi, \pi^*$ ) excited states of aromatic carbonyl compounds is concerned with the much greater efficiency of intersystem crossing (that is  $S_1 \rightarrow T_1$  conversion) in the case of the former state. This follows because triplet states are the longest lived and most useful intermediates in organic photochemistry. Two factors contribute to the high probability of intersystem crossing between ( $n, \pi^*$ ) states as compared with that between ( $\pi, \pi^*$ ) states:

1. The initial  $n \rightarrow \pi^*$  excitation is partly forbidden, and hence the reverse transition will also be partly forbidden. Thus the lifetimes of  $S_1$  ( $n, \pi^*$ ) states tend to be greater than  $S_1$  ( $\pi, \pi^*$ ) states, and the probability of conversion to the  $T_1$  state becomes correspondingly higher for  $S_1$  and  $T_1$  states.
2. Energy separations between  $S_1$  and  $T_1$  states of the ( $n, \pi^*$ ) type are normally quite small (1500 to 5000  $\text{cm}^{-1}$ ), whereas those for the corresponding ( $\pi, \pi^*$ ) states are usually much larger (10 000 to 15 000  $\text{cm}^{-1}$ ).

For aromatic carbonyl compounds, including benzophenones and quinones, which have the lowest energy  $n \rightarrow \pi^*$  transitions, intersystem crossing is essentially quantitative. Carbonyl triplet states of the ( $n, \pi^*$ ) nature readily abstract hydrogen atoms from reactive substrates, such as alcohols and ethers, with high quantum efficiencies.

Two types of aromatic carbonyl compound give rise to lowest energy excited states not having ( $n, \pi^*$ ) character. Amino-substituted benzophenones, especially, para-substituted compounds, form excited states which are neither ( $n, \pi^*$ ) nor ( $\pi, \pi^*$ ) in character, but which are better described as "charge transfer" states. A typical case is provided by 4, 4'-dimethylaminobenzophenone (Michlers's ketone) which yields an excited-state structure as shown in Fig. 2.

Whether the charge transfer state is lower in energy than the corresponding ( $n, \pi^*$ ) triplet state depends largely on the solvent polarity. Whenever the degree of conjugation in aromatic carbonyl compounds is more extensive than for example, the  $\text{Ph}-C=O$  group, the lowest lying triplet excited states are frequently ( $\pi, \pi^*$ ) in character and such compounds do not readily undergo the classical photo-induced hydrogen abstraction with alcohols and ethers. Examples of this type of compound include fluorenone, xanthone, *p*-phenylbenzophenone, and  $\alpha$ - and  $\beta$ -naphthyl carbonyl compounds.

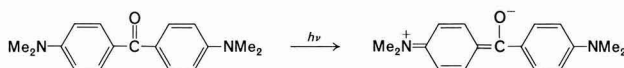


Fig. 2. Typical reaction to give "charge transfer" state

Whereas aromatic carbonyl compounds having lowest lying ( $\pi, \pi^*$ ) triplet excited states are not photo-reduced by hydrogen donors, such as alcohols and ethers, they are readily photo-reduced by electron donors, such as amines and sulfur compounds (see later discussion).

### Photo-induced fragmentation reactions of benzoin derivatives

Refs. 2-14

Among those aromatic carbonyl compounds which undergo fragmentation when irradiated with UV light, benzoin and benzoin alkyl ethers have been the most widely used as photoinitiators for vinyl polymerisation. Industrial applications of these compounds include the manufacture of printing plates (relief and dry offset) and the formulation of printing inks and surface coatings, the curing of which may involve the light-induced copolymerisation of unsaturated polyesters with styrene.

In the first detailed study of benzoin-photoinitiated polymerisation of vinyl monomers (styrene, butyl acrylate, methyl acrylate and methyl methacrylate) Melville<sup>3</sup> obtained kinetic evidence for photochemical production of radicals from benzoin. This was assumed to proceed by a Norrish Type I cleavage (Fig. 3). Recent CIDNP experiments<sup>4</sup> support this view, since it was observed that the radical pair formed on irradiation of benzoin was identical with that formed on irradiation of benzaldehyde.

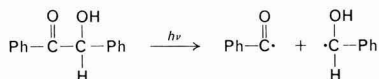


Fig. 3. Photochemical production of radicals from benzoin, assumed to proceed by a Norrish Type I cleavage

Further evidence for Type I cleavage has been obtained by the use of diamagnetic radical scavengers (I and II) as spin traps for radicals produced on photolysis of benzoin and benzoin methyl ether<sup>5</sup>. In both cases,  $\text{Ph}\dot{\text{C}}\text{O}$  and  $\text{Ph}\dot{\text{C}}\text{HOR}$  ( $\text{R}=\text{H}, \text{Me}$ ) radicals were trapped and characterised from the ESR spectra of the stable nitroxide radicals formed (Fig. 4). (These reactions are somewhat analogous to addition of the radicals to vinyl monomers.)

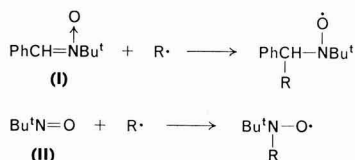


Fig. 4. Diamagnetic radical scavengers (I and II), used as spin traps for the radicals produced on the photolysis of benzoin and benzoin methyl ether, to provide further evidence for Type I cleavage

Similar results were obtained for reactions carried out in benzene and in methanol, those in the latter showing that fragmentation of photo-excited benzoin and benzoin methyl ether occurs much more rapidly than hydrogen abstraction from methanol.

Heine<sup>2,6</sup> isolated the products formed on photolysis of benzoin alkyl ethers (methyl, ethyl, isopropyl) in benzene, and these too were indicative of the intermediacy of benzoyl and alkoxybenzyl radicals (Fig. 5).

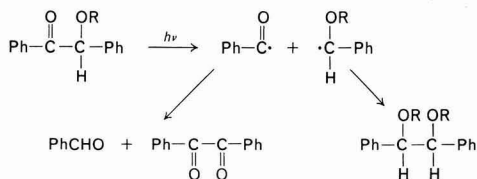


Fig. 5. Products formed by the photolysis of benzoin alkyl ethers in benzene

The efficiencies of benzoin derivatives in promoting the light-induced hardening of styrene-containing unsaturated polyester resins have been found to vary considerably<sup>2</sup>, benzoin alkyl ethers and  $\alpha$ -alkylated benzoines being more reactive than benzoin itself. As photoinitiators for the polymerisation of bulk methyl methacrylate, however, benzoin and benzoin methyl ether exhibit comparable efficiencies<sup>7</sup>, and this tendency is also indicated for the polymerisation of methyl acrylate in tertiary-butanol<sup>8</sup>. The relative photoinitiating efficiencies of benzoin derivatives can be influenced by several factors, some of which will depend on the nature of the monomer system and the environment in which the polymerisations are carried out. In addition, there are well defined differences in light absorption characteristics of benzoin and its alkyl ethers, which must be taken into account when assessing relative initiator efficiencies<sup>7</sup>.

Experiments involving triplet-state quenchers, for example piperylene, led Heine *et al.*<sup>6</sup> to the conclusion that whereas benzoin ethers fragment from singlet-excited states, benzoin itself fragments mainly from the triplet state. This could result in the latter's exhibiting higher quantum efficiencies for fragmentation in monomers having high triplet energies than it would in low triplet energy monomers (for example, styrene,  $E_T=255 \text{ kJ}$ )<sup>9</sup> where triplet-triplet energy transfer may compete with fragmentation of the excited benzoin. Quantum yields for photoinitiation by benzoin derivatives are typically in the range 0.2-0.3.

Norrish Type I cleavage of benzoin, benzoin alkyl ethers and  $\alpha$ -alkylated benzoines will in all cases give rise to benzoyl radicals. There is evidence<sup>10</sup> that the unpaired electron of the benzoyl radical is not delocalised into the aromatic nucleus; benzoyl radicals are expected, therefore, to be reactive species and efficient initiators. The fate of the more stable substituted benzyl radicals  $\text{Ph}\dot{\text{C}}\text{-OR}_2$  is less certain. For  $\text{R}_2=\text{H}$ ,

initiation by hydrogen transfer to monomer is a possibility<sup>2</sup> and has been proposed by Braun<sup>11</sup> for initiation of vinyl polymerisation by semibenzopinacol radicals,  $\text{Ar}_2\dot{\text{C}}\text{-OH}$ , generated by thermolysis of benzopinacols. However the comparable efficiencies of benzoin and benzoin methyl ether for bulk methyl methacrylate polymerisation<sup>7</sup> show that in this system, no marked effects arise from possible differences in reaction pathways open to  $\text{Ph}\dot{\text{C}}\text{OH}$  and  $\text{Ph}\dot{\text{C}}\text{OME}$  radicals. From the relationships between rate of polymerisation and number-average molecular weight of the polymers formed in the benzoin- and benzoin methyl ether-photo-initiated methyl methacrylate polymerisations, it was concluded<sup>7</sup> that primary radical termination of polymer chains did not occur to any significant extent. This may be taken as indirect evidence that both  $\text{Ph}\dot{\text{C}}\text{OH}$  and  $\text{Ph}\dot{\text{C}}\text{OME}$  radicals do in fact initiate polymerisation of this monomer.

Perhaps the most informative study of photoinitiation by benzoin methyl ether is that reported recently by Pappas and

Chattopadhyay<sup>12</sup>, who studied the polymerisation of bulk methyl methacrylate, photo-induced by benzoin methyl ether <sup>14</sup>C-labelled successively in the methyl ether group, the benzoyl fragment and the  $\alpha$ -methoxybenzyl radical fragment. Incidentally, this study refutes an earlier claim<sup>13</sup> that 12 to 14 moles (or radio-active fragments) of initiator are incorporated per mole of polymer. Pappas and Chattopadhyay<sup>12</sup> found that the system exhibited conventional polymerisation behaviour with regard to kinetics, for initiation by both benzoyl and  $\alpha$ -methoxy benzyl radicals. For initiator concentrations such that only 14 per cent of the incident light was absorbed, termination was by disproportionation and at least 85 per cent of the light quanta absorbed led to initiation of polymer chains. In contrast, when the initiator concentration was increased so that all the incident light was absorbed, the quantum efficiency for initiation was only about 25 per cent and molecular weights were much lower—clear evidence for primary radical termination. These results should suffice to illustrate the difficulties of making comparisons of initiator efficiencies, unless extensive care is taken to standardise the conditions in respect of light absorption characteristics, solution viscosity, etc.

More recently, a significant development related to benzoin ether photolysis has been a demonstration, by workers in the Union Carbide Laboratories<sup>14</sup>, of the very high efficiencies in photoinitiation of 2,2-diethoxyacetophenone (DEAP) and 2,2-dimethoxy-2-phenylacetophenone (DMPA). For the

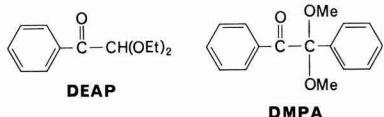


Fig. 6. Structure of 2,2-diethoxy acetophenone (DEAP) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA)

polymerisation of 2-ethylhexyl methacrylate, these compounds were substantially better than benzoin alkyl ethers, and it has been suggested that secondary fragmentation of the alkoxy alkyl radicals might be a process competing with radical combination reactions (including termination of polymerisation) and hence might give rise to higher overall efficiencies in radical polymerisation (Fig. 7).

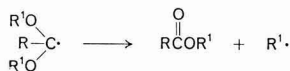


Fig. 7. Secondary fragmentation of an alkoxy alkyl radical

### Photoinitiation by benzophenone derivatives

Refs. 15-35

The best known hydrogen abstraction reaction of aromatic carbonyl compounds is that involved in the formation of benzopinacol upon ultraviolet irradiation of solutions of benzophenone in ethers and alcohols. This has been the subject of a large number of studies<sup>15-21</sup> and quantum yields for photoreduction<sup>21</sup> approach a value of two, that is approximately two molecules of benzophenone are consumed per quantum of light absorbed. The reaction is generally

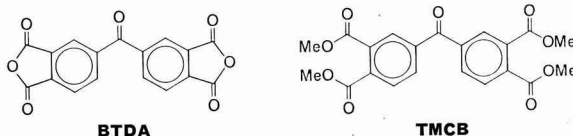
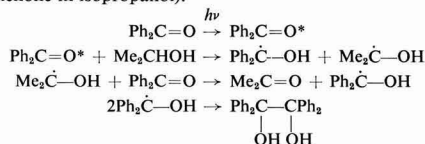


Fig. 9. Structures of: 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3',4,4'-tetramethoxycarbonyl benzophenone (TMCB)

considered to proceed via free radical intermediates according to the scheme shown below<sup>18</sup> (for photoreduction of benzophenone in isopropanol).



Photoreduction of benzophenone by isopropanol is accompanied by the formation of a coloured compound, which Filipescu and Minn<sup>19</sup> proposed was an adduct of the radicals resulting from hydrogen abstraction (Fig. 8). These authors further proposed that this adduct was a key intermediate in the photoreduction process, semi-pinacol radicals being generated by its reaction with ground-state benzophenone.

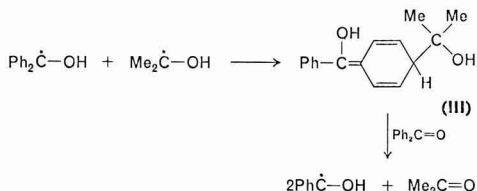


Fig. 8. Photoreduction of benzophenone by isopropanol, and subsequent formation of radicals resulting from hydrogen abstraction

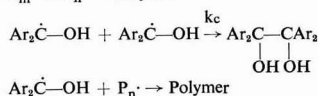
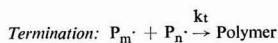
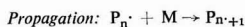
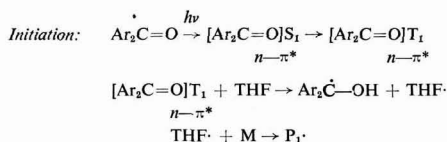
The precise reaction mechanism is still a matter of controversy. Weiner<sup>20</sup> has pointed out that the proposition that the coloured compound (III) is a key intermediate cannot be reconciled with available kinetic data, and considers its formation to be incidental to the production of benzopinacol. Weiner<sup>20</sup> has also reported evidence for formation of a "direct" adduct,  $\text{Ph}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Me}_2$ , which apparently arises from an "in-cage" reaction, accounting for approximately 10 per cent of the radical intermediates.

Initial formation of radicals by photo-induced hydrogen abstraction from the substrate is not in dispute and, as noted earlier, hydrogen abstraction from alcohols, ethers and hydrocarbons is effected with high quantum efficiencies by aromatic carbonyl compounds in which the lowest lying triplet level is of  $n-\pi^*$  type, for example, benzophenone, anthraquinone<sup>22-24</sup>.

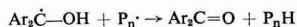
Photo-induced hydrogen abstraction by benzophenone has been utilised for the grafting of styrene on to polyethylene<sup>25</sup>, acrylamide on to polyethylene<sup>26</sup>, acrylamide on to natural rubber<sup>27</sup>, methacrylamide on to cellulose triacetate film<sup>28</sup>, for the photodegradation of polyvinyl chloride<sup>29</sup>, polyvinyl alcohol<sup>30</sup> and polyurethanes<sup>31</sup>, and for the photocrosslinking of polyethylene<sup>32</sup>. Regrettably, there are few mechanistic details of any of these processes available, and the only report giving full information as to relative efficiencies and mechanism is that of Block, Ledwith and Taylor<sup>33</sup> who studied homopolymerisation of methyl methacrylate in tetrahydrofuran solvent (and hydrogen donor) photo-induced by benzophenone (BP), 3,3',4,4'-benzophenone tetracarboxylic dian-

hydride (BTDA), and 3,3',4,4'-tetramethoxycarbonyl benzophenone (TCMB).

Efficiencies increased in the order: benzophenone < TCMB < BTDA, although the ultraviolet absorption spectra of these compounds showed only minor variations in the region 330-380 nm. The kinetic results were consistent with the expected free radical mechanism, polymerisation rates being half-order with respect to the concentrations of the benzophenones. However, the viscosity-average molecular weights of the resulting polymers were considerably less than those measured for polymers formed at comparable rates, at the same temperature, using azobisisobutyronitrile as photoinitiator (again in tetrahydrofuran solution). The effect was most pronounced in the case of polymerisations photoinitiated by benzophenone itself, and indicated the participation of an extra termination or transfer step. It was concluded that the reduction in molecular weight of polymers formed in the reactions photoinitiated by benzophenones was caused by an intermediate formed in the initiation process. The presence of a solvent with readily abstractable hydrogen atoms was shown to be essential for efficient photoinitiation by benzophenone; in benzene (a poor hydrogen donor), the rate of photo-induced polymerisation of methyl methacrylate was only marginally increased by the presence of benzophenone, and the experimental observations were consistent with the reaction scheme shown below.



Relative efficiencies of the three benzophenone derivatives, and the sequence observed in the (polymer molecular weight)/(polymerisation rate) relationships, could be due to differing tendencies of the respective semi-pinacol radicals to undergo self-combination, since it seems reasonable to assume that semi-pinacol radicals should show rather small differences in their abilities to combine with growing polymer radicals. It was pointed out, however, that this termination reaction may involve hydrogen transfer rather than direct combination:



and hence differences in the efficiency of hydrogen transfer from the semi-pinacol radicals could be an alternative explanation for the experimental observations noted above<sup>33</sup>. More recently, Hammond and his collaborators<sup>34</sup>, using a combination of flash photolytic and ESR techniques, have investigated in considerable detail the rates of recombination of semi-pinacol radicals ( $p\text{-XC}_6\text{H}_4$ )<sub>2</sub>C<sup>·</sup>-OH where X=H, OMe, Cl. A most important conclusion from these studies was that whilst in purely alkane solvents, rates of recombination of the semi-pinacol radicals were essentially diffusion controlled, the corresponding reactions in solvents, such as benzene or isopropanol, exhibited a pronounced effect of substituent X on reaction rate. Clearly then, relative rates of self-combination of semi-pinacol radicals, or of combination with growing

polymer radicals (termination), could be different according to the nature of substituents and any specific or general solvation forces between solvent, monomer and the reacting radicals.

Another factor which could influence the photoinitiating efficiencies of benzophenone derivatives is the extent of in-cage reaction of the primary radicals, resulting from hydrogen abstraction. Cage reactions reported to occur in the photo-reduction of benzophenone by isopropanol have already been described. Photolysis of benzophenone in tetrahydrofuran was found<sup>35</sup> to cause an increase in the ultraviolet absorption spectrum between 300 and 370 nm. This was ascribed to the formation of an adduct arising from combination of semi-pinacol and tetrahydrofuran-derived radicals, and analogous in structure to that proposed by Filipescu and Minn<sup>19</sup>. The presence of increasing proportions of methyl methacrylate (in the range 0-50 per cent by volume) resulted in a corresponding decrease in the rate of formation of the adduct. Two possible mechanistic interpretations of this were offered:

- (i) The quantum yield for production of the primary radicals is not altered by addition of methyl methacrylate, but the proportion of tetrahydrofuran-derived radicals which react with methyl methacrylate increases with increasing concentration of the latter; thus the rate of adduct formation is decreased.
- (ii) The proportion of primary radicals which combine to give adduct remains constant, but the overall rate of primary radical formation decreases with increasing methyl methacrylate concentration owing to quenching of triplet-excited benzophenone by methyl methacrylate.

In the benzophenone-photoinitiated polymerisation of methyl methacrylate, interpretation (i) would tend to increase the order of reaction with respect to monomer concentration, whereas interpretation (ii) would tend to decrease this, assuming that the species formed as the result of quenching initiated polymerisation less efficiently than the solvent-derived radicals. The data of Block *et al*<sup>33</sup> give a value of 0.84 for the order in monomer, and it could be argued that this is significantly lower than the value of unity predicted by the suggested kinetic scheme, and favours interpretation (ii). Values obtained for monomer orders in the case of the BTDA- and TCMB-photoinitiated polymerisations were much closer to unity (1.02 and 0.98 respectively) which, following the present reasoning, would indicate that the excited states of these derivations are not quenched by methyl methacrylate.

Thus the relative photoinitiating efficiencies of benzophenone derivatives may be influenced by whether or not their photo-excited states are quenched by monomer, and the fraction of in-cage combination of the radicals formed by hydrogen abstraction, as well as the extents to which the respective semi-pinacol radicals terminate polymer chains. At elevated temperatures, differences in the initiating abilities of the semi-pinacol radicals must also be considered.

## Photoinitiation by quinones

*Refs. 22-24, 36-55*

Quinones are a special case of aromatic carbonyl compound and, in general, give lowest lying excited states having ( $n, \pi^*$ ) character. This means that photo-induced hydrogen abstraction processes are as common for triplet quinones as for benzophenone derivatives. Anthraquinone<sup>22-24</sup> and its derivatives<sup>36-41</sup> have mostly been studied from this point of view, but there are several reports of photoreduction of other quinones<sup>42-44</sup>. Generally, the types of hydrogen donor

molecules (alcohols, ethers) effective for photoreduction of quinones are the same as for benzophenones and reaction mechanisms are very similar. One difference between quinones and benzophenones is that the former more readily yield anionic radicals on reduction, particularly in alkaline media. A further point of difference between photoreactions of quinones and benzophenones is the much greater and often useful involvement of intermediate peroxy compounds in reactions of the former, when conducted in air<sup>45-47</sup>.

There are numerous references in the Patent literature<sup>48-52</sup> to the use of anthraquinone (AQ) and similar compounds as photoinitiators of polymerisation or crosslinking required in the preparation of printing plates etc, although it appears that little is known of the detailed reaction mechanisms. One literature report<sup>53</sup> describes the polymerisation of aqueous methyl acrylate by sodium anthraquinone-2-sulfonate in the presence of chloride ions, with a conclusion that the initiating species are chlorine atoms.

A comprehensive study of the free radical polymerisation of methyl methacrylate (MMA) photoinitiated by anthraquinone (AQ) and 2-tert-butyl anthraquinone (TBAQ) in tetrahydrofuran (THF) has been completed by Ledwith, Ndaalio and Taylor<sup>54</sup>. TBAQ is frequently used in applications on account of its greater solubility and compatibility with solvents and polymers, but detailed studies of kinetics and mechanism<sup>54</sup> show that AQ and TBAQ behave in an almost identical manner. Of particular value in interpreting detailed mechanisms in these systems were the spectral changes noted during polymerisation. Irradiation of AQ in THF without monomer gave rise to a blue fluorescing product with absorption maxima at 400 and 374 nm, similar to photo-adducts from THF and other quinones<sup>55</sup>. In the presence of polymerisable monomer, however, the solutions developed a characteristic blue-green fluorescence with an absorption spectrum ( $\lambda_{\text{max}}$  383 nm) identical to that reported<sup>23</sup> for anthrahydroquinone. The latter product rapidly reached a comparatively low, constant concentration during polymerisation, and both this material and the adduct formed in high conversion by the photolysis of AQ in THF without monomer, were immediately destroyed by exposure to atmospheric oxygen. A reaction scheme consistent with the experimental observations is indicated (in Fig. 10).

The proposed reaction scheme assumes that the observed steady-state concentration of anthrahydroquinone (AQH<sub>2</sub>) results from competition between disproportionation of the initially formed semiquinone radical, and termination of polymer chains by AQH· and by anthrahydroquinone (with regeneration of AQH·). In this way it is possible to explain the observed enhanced efficiency of anthraquinones as photoinitiators when used in the presence of dissolved air or oxygen. Presumably, oxygen would serve constantly to maintain the concentration of photoinitiating quinone by rapid reaction with AQH· and AQH<sub>2</sub>. Peroxy radicals formed during these processes may also contribute to initiation of polymerisation. In this respect, anthraquinone systems differ markedly from those involving benzophenones where dissolved oxygen has a marked retarding influence.

### Photoinitiation by electron transfer processes

Refs. 8, 56-69

It is now well recognised that aromatic carbonyl compounds may be efficiently reduced by a variety of electron donor molecules, especially amino compounds, irrespective of whether the excited state undergoing reaction is ( $n$ ,  $\pi^*$ ) or

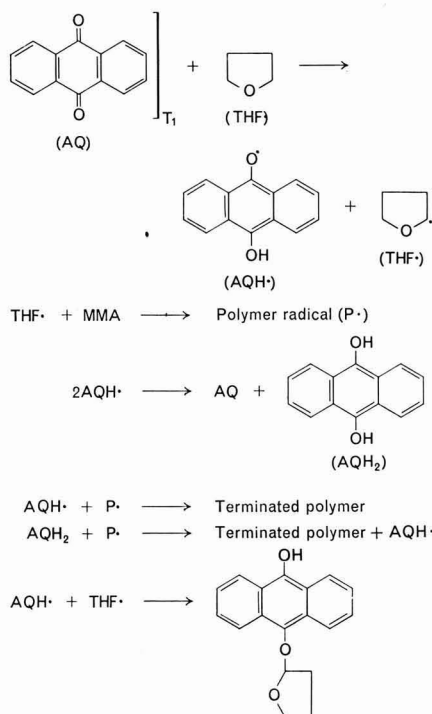
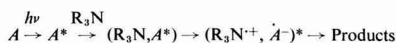


Fig. 10. Proposed reaction scheme (consistent with experimental observations) for the irradiation of anthraquinone in tetrahydrofuran

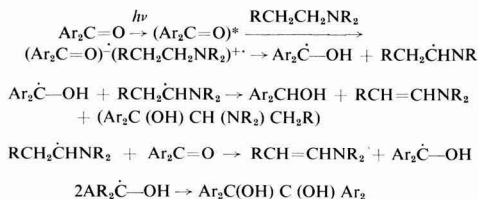
( $\pi$ ,  $\pi^*$ ) in nature. A full account of photoreduction of aromatic ketones by amines has been given by Cohen, Parola and Parsons<sup>56</sup> and it can be seen that these reactions constitute just one class of a wider range of photoreactions of amino compounds occurring via formation of encounter complexes or "exciplexes". Denoting aromatic carbonyl compound or condensed aromatic molecule, etc by  $A$ , photo-oxidation of amines may be generalised thus:



Of particular interest here are the processes whereby encounter complexes ( $R_3N, A^*$ ) and exciplexes ( $R_3N^+, \dot{A}^-$ ) may give rise to the formation of free radicals active in initiation of vinyl polymerisations<sup>57</sup>.

Singlet and triplet states of aromatic ketones are efficiently quenched by a wide variety of amino compounds and a general correlation exists between quenching efficiency and ionisation potential of the amine, for a particular class of amine<sup>56</sup>. In many cases tertiary amines are more effective than corresponding secondary and primary derivatives, although specific solvation phenomena may change this order of reactivity. Benzophenone, no less than any other aromatic ketone, is efficiently reduced by amines in a variety of solvents at rates which are substantially faster than those observed for corresponding photo-induced hydrogen abstractions from, say, alcohols<sup>58</sup>. Products from these various photo-redox processes are related, and for the photo-oxidation of amines, may be generalised as follows:





Sandner *et al*<sup>6</sup> observed that the addition of small amounts of triethylamine (0.02M) greatly enhanced the photo-induced polymerisation of methyl acrylate (1.0M in tertiary-butanol, nitrogen-flushed) in the presence of benzophenone (0.02M). Photoinitiation was not effected by triethylamine alone, nor by triphenylamine, isopropanol, or benzhydrol (all 0.02M) in the presence of benzophenone. Quantum yields, measured for disappearance of benzophenone, indicated that methyl acrylate itself acted as a quencher of photo-excited benzophenone, effectively suppressing hydrogen abstraction from tertiary-butanol, and benzhydrol. However, this quenching action had only a marginal effect on the efficiency of interaction of photo-excited benzophenone with triethylamine, suggesting that something other than direct hydrogen abstraction from the amine was involved. Consistent with this view was the observation that triphenylamine inhibited photoreduction of benzophenone in tertiary-butanol. Efficient formation of an excited electron-transfer complex from triplet benzophenone and ground-state amine was postulated, but initiation by the complex itself, perhaps by an anionic pathway, was discounted in view of the ineffectiveness of triphenylamine as co-initiator. In the case of triethylamine, it was proposed that initiating radicals resulted from collapse of the complex, following proton transfer as illustrated above.

In the author's own work, the use of ketones thought to possess the lowest ( $\pi$ ,  $\pi^*$ ) triplet excited states has been preferred, because (although the point is still uncertain in some cases) ( $\pi$ ,  $\pi^*$ )-excited triplets do not generally undergo direct hydrogen abstraction reactions with alcohols, alkanes, etc. Fluorenone (FLO) is undoubtedly the most useful of the aromatic ketones having lowest lying ( $\pi$ ,  $\pi^*$ ) triplet excited states and its photophysical characteristics have been extensively studied by several workers<sup>59-61</sup>.

Photoreduction of fluorenone does not occur in alcohol, ether or alkane solvents, but occurs readily in the presence of amines, with tertiary amines being most effective<sup>62, 63</sup>. A rather special feature of the photochemistry of fluorenone is the dramatic effect of solvent on the rates of intersystem crossing from singlet to triplet manifolds. Although a detailed explanation of this phenomenon is still lacking, the generalisation may be made that increasing solvent polarity decreases the facility for intersystem crossing and simultaneously increases the quantum yield for fluorescence. Thus triplet state activity is maximised in solvents, such as benzene and cyclohexane, for which the values of triplet yields<sup>64</sup> are 0.93 and 1.03 respectively. In contrast, triplet yields in solvents, such as alcohols, acetone, acetonitrile, are substantially less than unity with a concomitant increase in quantum yields for fluorescence. Ionisation potentials of amines are important in determining quenching ability for both singlet- and triplet-excited fluorenone, but it now appears that photoreduction is consequent upon interaction of triplet excited fluorenone with amine donors<sup>56</sup>, the main effect of singlet state quenching being to reduce triplet yields. Experimental observations from several workers may be summarised, therefore, by stating that photoreduction of fluorenone by

amines occurs most readily in solvents such as benzene and cyclohexane, and only with low quantum efficiency in solvents, such as acetone and acetonitrile. A further complication arises because the amines themselves may be regarded as polar additives (in comparison with hydrocarbons) and hence there is a marked effect of amine concentration on photoreduction of fluorenone in hydrocarbon solvents. For example, quantum yields for photoreduction of fluorenone by triethylamine have been measured as 0.09 in neat amine, 0.9 in 0.1M amine (in cyclohexane) and 0.6 in 0.02M amine<sup>56</sup>. That electron transfer is involved in these quenching and photoreduction processes is indicated not only by the clear dependence on ionisation potential of the donor amine, but also by flash photolytic and ESR characterisation of ion radical intermediates—especially for those systems where the quencher has no readily abstractable hydrogen atom.

The kinetics of photo-induced polymerisation of methyl methacrylate in the presence of fluorenone (FLO) and N,N-dimethyl ethanolamine (DME) have been studied in some detail<sup>57, 65</sup>. The experiments were carried out at 30°C, using de-gassed solutions sealed under high vacuum, and employing a 250W medium-pressure mercury discharge lamp as the source of ultraviolet light. Polymerisation rates exhibited half-order dependencies on incident light intensity and fluorenone concentration (in the range from zero to  $1.5 \times 10^{-4}$ M), and were first-order with respect to monomer concentration, as determined from initial rates measured for various concentrations of methyl methacrylate in benzene; thus a radical chain mechanism was indicated.

As a function of N, N-dimethyl ethanolamine concentration, the polymerisation rate passed through a maximum, corresponding to the behaviour in photoreduction of fluorenone by other tertiary amines, as noted above. Molecular weight determinations in the FO/DME/MMA system give a value for  $k_p/k_t^{0.5}$  equal to  $0.054 \text{ mol}^{-0.5} \text{ s}^{-0.5}$  indicating that transfer and termination processes are not particularly affected by the initiating components or their photoredox products. Almost all tertiary amines having  $\alpha$ -hydrogen atoms may be used conveniently, and other carbonyl compounds, notably N-methyl acridone (NMA) which has a much higher molar extinction coefficient than fluorenone, are also effective (Fig. 11).

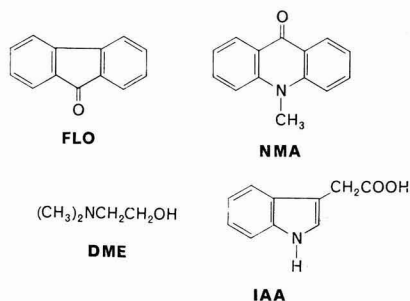


Fig. 11. Structures of: fluorenone (FLO); N-methyl acridone (NMA); N,N-dimethyl ethanolamine (DME); and indol-3-yl-acetic acid (IAA)

The scope of this initiation reaction may be widened by using an arylamino-acetic acid derivative as the electron donor, with the same sensitizers, and of these indol-3-yl-acetic acid (IAA) is experimentally convenient. In these cases, it is thought that the initiating radicals arise via decarboxylation following the normal photo-induced electron transfer. Quantum yields for initiation by the combination FLO/DME,



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# The technological literature relating to polymerisation photoinitiators\*

By A. Pryce

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## Summary

The literature relating to the development of photoinitiators for polymerisation on exposure to ultraviolet light is reviewed. The types of photoinitiator considered are benzoin and its derivatives,

benzoin ethers, benzil, and aryl diazonium salts. References are given to work on a number of other photosensitisers.

## Keywords

*Processes and methods primarily associated with:*

*manufacturing or synthesis*

*photoinitiation*

*drying or curing of coatings*

*photoinitiation*

*photopolymerisation*

*ultraviolet curing*

## La littérature technique sur les photoinitiateurs de polymérisation

### Résumé

On passe en revue la littérature sur l'évaluation des photoinitiateurs de polymérisation par exposition à la lumière ultra violette. Les types de photoinitiateurs étudiés comprennent benzoïne et ses

dérivés, éthers de benzoïne, benzile, et les sels d'aryles diazotiques. On fait référence aux études sur un certain nombre d'autres photosensibilisateurs.

## Die sich auf Polymerisationsphotoinitiatoren beziehende technologische Literatur

### Zusammenfassung

Die sich auf die Entwicklung von Photoinitiatoren zur Polymerisierung bei ultraviolettem Licht beziehende Literatur wird besprochen. Die hierfür in Betracht gezogenen Photoinitiatortypen

sind Benzoin und seine Derivate, Benzoinäther, Benzil und Aryldiazoniumsalze. Auf Arbeiten mit einer Anzahl anderer Photosensibilisatoren wird hingewiesen.

## Introduction

*Ref. 1*

The use of UV-curing polymers dates back to ancient Egyptian times, when mummies were wrapped in linen cloths dipped in a solution of "oil of lavender" containing a high-molecular weight bituminous material called "Syrian asphalt", a substance which became cross-linked on exposure to sunlight. The use of photosensitisers to increase rates of polymerisation, however, is a relatively modern practice and really became significant only after the second world war.

Uranyl nitrate, found to be a sensitiser for the polymerisation of vinyl chloride in sunlight<sup>1</sup>, was one of the earlier photosensitisers. Since it was first described in the literature, many surface coating and ink manufacturers have devoted much attention to photopolymerisable resins and to the photoinitiators required to give efficient polymerisation of monomers or cross-linking of prepolymers.

## Assessment of photoinitiators

*Refs. 2-4*

The requirements of a photoinitiator are:

- (i) Efficient absorption of UV-radiation energy and resultant production (by fragmentation or by hydrogen or electron abstraction) of polymerisation-initiating species (e.g. free radicals, Lewis acids, etc).

- (ii) No polymerisation initiation in the absence of light; that is, good thermal stability.

Two recent papers have dealt with methods of comparing the kinetics of UV-initiated polymerisation. A dilatometric method<sup>2</sup> relied on the change in volume which accompanies polymerisation, to indicate the degree of polymerisation. This method may be used for comparing the relative efficiencies of photoinitiators, photopolymerisable monomers, UV sources and inhibitors. The second paper<sup>3</sup> covered a study of the effect of UV-lamp irradiance on the speed of cure of photopolymers, a quartz probe being used to measure irradiance: this study concluded that irradiance had a more marked effect on speed of cure than did exposure time. Other workers<sup>4</sup> have studied the polymerisation of an unsaturated polyester-styrene composition by monitoring the free styrene present after exposure for various times; the conclusions, as expected, were that less free styrene remained as the exposure time was increased or film thickness decreased, or when the distance between lamp and coating was reduced, or the initiator concentration increased.

The most convenient method for comparing photoinitiators is by means of a laboratory-scale exposure unit, where the sample is passed under a high pressure mercury lamp (79 watts per linear cm output) by means of a variable speed conveyor belt. A commercially available apparatus of this type is the Primarc "Minicure" apparatus, available from Primarc (Jigs & Lamps) Ltd, Henley-on-Thames, England.

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



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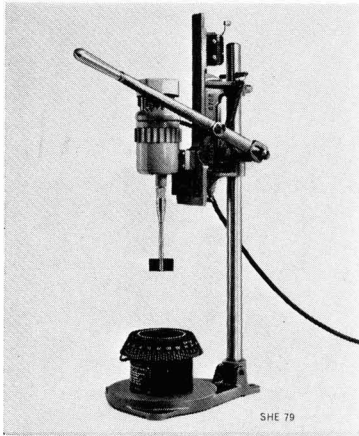
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Once satisfactory rates of cure have been obtained with the photoinitiator, it is necessary to ensure that the formulation does not gel in the can upon standing. This "dark storage stability" testing is usually accelerated by storing at 60°C and periodically inspecting the samples, which should preferably be kept in sealed containers.

Some photoinitiators which have achieved commercial significance are covered in the following review of the technological literature, but little attempt has been made to interpret the theoretical considerations which govern their efficiency.

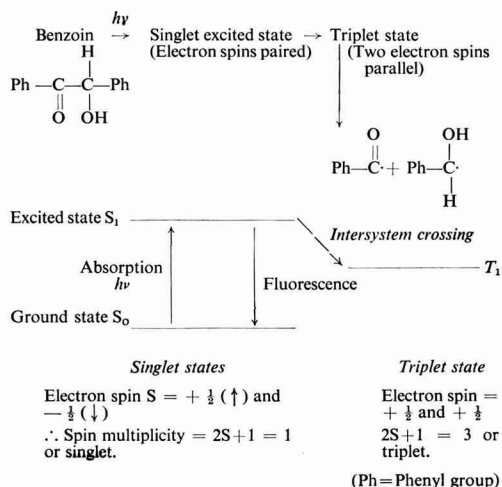
## Benzoin and its derivatives

Refs. 5-19, 75, 76, 14b

Benzoin and its derivatives were among the earliest patented initiators for photopolymerisation and have received much attention in the technological literature.

### Benzoin

The mode of action of benzoin as a photoinitiator is thought to be dissociation of the excited triplet state to form free radicals:

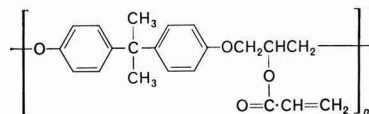


Patents issued to du Pont de Nemours<sup>5</sup> in 1945 concerned the use of benzoin as a photoinitiator for vinyl monomers in a composition for sealing "Perspex" bomber turrets. Later patents by du Pont also claimed benzoin<sup>6</sup> and  $\alpha$ -alkyl benzoin<sup>7</sup> as photoinitiators; the latter is stated to give increased rates of cure. This early commercial interest in benzoin has waned considerably, with less frequent mention of it in recent years<sup>8, 9</sup>, despite the results of Ledwith<sup>10</sup>, which revealed a high photoinitiating efficiency in the polymerisation of methyl methacrylate, and those of Czechoslovak workers<sup>11</sup>, who compared a large number of benzoin derivatives in an unsaturated polyester/styrene system. The main disadvantage of benzoin appears to be the poor dark-storage stability of UV-polymerisable compositions<sup>11</sup>, but a Japanese patent<sup>12</sup> claims greatly improved dark storage stability (10 days as compared with one day at 60°C) for a polyester/styrene composition by preparing the polymer in the presence of the benzoin. The  $\alpha$ -substitution of benzoin with C<sub>1-8</sub> alkyl groups

has enabled the formulation of styrene-unsaturated polyester compositions<sup>13</sup> containing small amounts of (RO)<sub>3</sub>P and copper compounds: these compositions have storage stability for several months.

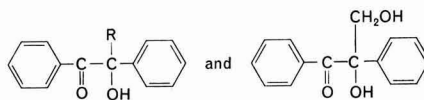
Benzoin has been reacted with various monomers which were then polymerised to give photosensitive cross-linking polymers, for example, with acryloyl chloride<sup>14</sup>. Benzoin with diisocyanate and a vinyl monomer containing -OH, -COOH, or -NH<sub>2</sub> groups gives photopolymerisable monomers<sup>15</sup>.

The use of benzoin in combination with *p*-phenylene diamine<sup>16</sup> and with Michler's ketone<sup>17</sup> have also been the subject of patents. The sensitivity of an acryloyl-substituted polyhydroxy ether:

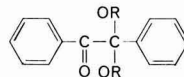


in the presence of a synergistic mixture of benzoin and Michler's ketone was shown to extend up to a wavelength of 420 nanometres<sup>14b</sup>.

In the quest for improved performance, modifications to the benzoin molecule have included  $\alpha$ -alkylation<sup>18</sup> and  $\alpha$ -methylation<sup>19</sup>, that is:



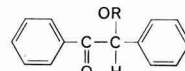
The latest innovations to appear in the literature<sup>75, 76</sup> are benzil ketals:



### Benzoin ethers

Refs. 20, 10, 11, 24-48, 32a, 85, 27b, 49, 4, 50-69

The ethers of benzoin, of general formula:



have been known to chemists since the nineteenth century. Whereas benzoin itself fragments into free radicals from the excited triplet state, its ethers are believed to fragment directly from singlet-excited states<sup>20</sup>. They may, therefore, be expected to show efficiencies different from benzoin in photopolymerisable systems. Styrene-unsaturated polyester systems are initiated more efficiently by benzoin alkyl ethers than by benzoin<sup>20a, 11</sup>, but as photoinitiators for bulk methyl methacrylate<sup>10</sup> or methyl acrylate<sup>21</sup> in butanol, the efficiencies for benzoin and its ethers are more similar.

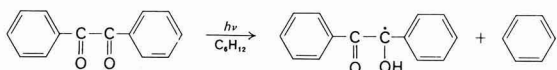
Benzoin ethers were patented in the 1940s by du Pont<sup>22</sup>, who made the dubious claim<sup>23</sup> that benzoin methyl ether (BME) gave thermally stable polymerisable compositions below 85°C. This claim has been disproved by later workers<sup>11</sup>, who have experienced poor dark storage stability with compositions containing BME—although a considerable improve-

ment is obtained by using higher alkyl ethers, such as butyl ethers of benzoin.

Since 1960, benzoin ethers have been mentioned in patents covering photopolymerisation of the following systems:

- (i) Unsaturated polyester/vinyl monomers<sup>24, 31</sup>
- (ii) Unsaturated polyamides/vinyl monomers<sup>32</sup>
- (iii) Multi-functional acrylate monomers<sup>33, 34</sup>, for example trimethylol propane triacrylate<sup>35</sup>
- (iv) Cellulose fibres/acrylic monomer<sup>36</sup>
- (v) Polybutadiene oligomers/vinyl containing esters<sup>37</sup>
- (vi) Polyurethanes<sup>38</sup>
- (vii) Acrylamide/acrylonitrile or acrylic acid copolymers<sup>39</sup>
- (viii) Air-drying lacquers<sup>40, 41</sup>
- (ix) Isocyanate-modified acrylic prepolymers<sup>42, 43</sup>
- (x) Acrylic-modified epoxy resins<sup>44, 48</sup>

The problem of dark storage stability has also occurred with some photopolymerisable compositions. The inclusion of polymerisation inhibitors, for example hydroquinone<sup>32a</sup> or its methyl ether<sup>53</sup>, or tertiary butyl pyrocatechol<sup>27b, 49</sup>, has solved this problem in some cases. A report<sup>4</sup> that the addition of 0.01 per cent of the inhibitor toluene hydroquinone had no deleterious effect on the rate of cure of unsaturated polyester/styrene compositions indicates that efficient conversion of the photoinitiator to free radicals upon UV-irradiation completely swamps the inhibitor. Improved results were claimed by additions of methyl-*p*-benzoquinone<sup>51</sup> (at 0.01 per cent, on total) with benzoin butyl ether (at 1 per cent, on the resin). The improved dark storage stability obtained by increasing the alkyl chain length in the benzoin ethers is further increased by chain branching. Ethers derived



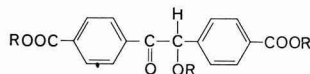
from secondary alcohols have better dark storage properties than those from primary alcohols<sup>52</sup>. Other additives which have been claimed to increase the stability of compositions containing benzoin ethers and in some cases cause a synergistic improvement in photoinitiating efficiency include:

- (i) Organic phosphines  $P(R)_3$  and phosphites  $P(OR)_3$  have been the subjects of patents<sup>53, 54</sup> and synergistic effects are obtained at ratios from 1:1 to 10:1 of benzoin ether: phosphine or phosphite. Triphenyl or tri-*o*-tolyl derivatives are preferred.
- (ii) Quaternary ammonium chlorides, such as benzil trimethyl ammonium chloride<sup>55</sup> are stabilisers for unsaturated polyesters.
- (iii) Organic acids, such as lactic, oxalic, citric<sup>56</sup>, benzoic<sup>50</sup> and tartaric acids<sup>57</sup>.
- (iv) Copper compounds, for example copper naphthenate or the addition product of trichloroethyl phosphite and cuprous chloride, were found to impart stability to benzoin ethers. Strangely, in the presence of these copper compounds, the ethers from primary alcohols are more stable than those from secondary alcohols<sup>58</sup>.
- (v) Iron, manganese or copper compounds soluble in polyester resins (for example, naphthenates and octoates), and organic compounds having ionically bound chlorine, for example quaternary ammonium chlorides<sup>59</sup>. The quater-

nary compound should contain sufficient alkyl substituents to ensure solubility in the resin.

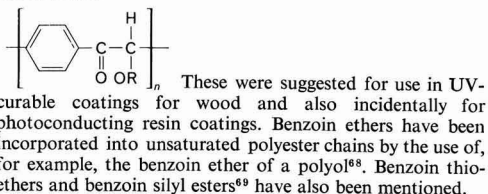
- (vi) Diethylhydroxylamine<sup>60</sup>.

Many variations on the benzoin ether theme have been the subjects of patents over the past few years. The phenyl rings have been substituted with alkoxy-carbonyls<sup>61</sup>, that is:



and also with a range of other substituents<sup>62</sup>. The aliphatic carbon atom adjacent to the ketone group has been alkylated<sup>63</sup>, methylated<sup>64, 65</sup> and methylol-sulfonated<sup>66</sup>.

Poly(benzoin ethers) have been described<sup>67</sup> which have the structure:



## Benzil

Refs. 70-77, 10, 14b

In contrast to benzoin and its ethers, benzil functions not by fragmentation but by hydrogen abstraction by the photo-excited benzil.

Benzil absorbs UV radiation at longer wavelengths than does either benzoin or its alkyl ethers (Fig. 1), so given efficient conversion to free radicals, benzil could offer advantages in speed

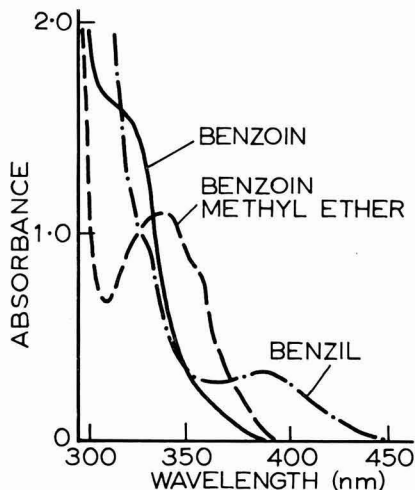


Fig. 1. Ultraviolet absorption spectra in methyl methacrylate



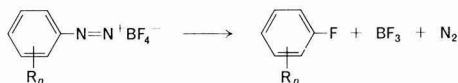
of cure. Early patents referred to benzil<sup>70,71</sup> and more recently an unsaturated polyester/styrene composition containing benzil<sup>72</sup> has been mentioned. Ledwith<sup>10</sup>, however, has concluded that benzil is less efficient than either benzoin or its methyl ether in photosensitising the polymerisation of methyl methacrylate. The activity of benzil is expected to be increased in the presence of a reducing agent, and a recent patent by one company suggests the use of dimethylaminoethylmethacrylate (DMAEMA), triethylamine, tributylphosphine, allyl thio-urea or similar reducing agents with benzil in an unsaturated polyester system<sup>73</sup>—low oxygen sensitivity and a dramatic improvement in cure rate was claimed for this system. A later patent, awarded to the same company, suggested the use of 28 per cent benzil and 4 per cent DMAEMA in acetone solution, on the composition<sup>74</sup>.

Synergism of benzil with Michler's ketone has been reported<sup>14b</sup>, and a combination<sup>77</sup> of benzil (2 per cent on resin), 22' thiobis(benzothiazole) (2 per cent) and *p*-dimethylaminobenzophenone (0.5 per cent) gave complete cure in 0.1 seconds of a methacrylated polyamide/methacrylic ester system pigmented with titanium dioxide.

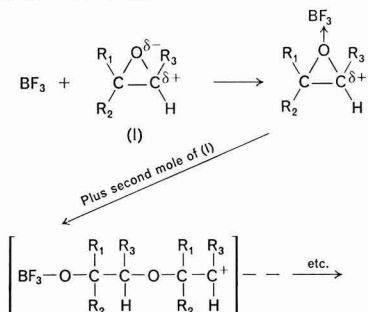
### Aryl diazonium salts

Refs. 78-84

The aryl diazonium salts have received considerable attention in the patent literature due to their release of Lewis acids on photolytic degradation. The diazonium salts of inorganic acids are used (fluoroborate salts, hexafluorophosphates etc), for example:



The Lewis acid  $\text{BF}_3$  initiates cationic polymerisation of, for example, epoxides<sup>78</sup> thus:



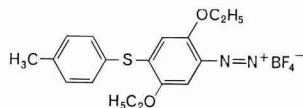
Electron withdrawing substituents on the benzene ring of the azo compound have been found to be advantageous. Design of these azo compounds to give optimum light sensitivity has been well developed for the so-called "dylene" photo-reproduction process (which is based upon destruction of diazonium compound in exposed area and then coupling of remaining diazo with, for example, phenols to give coloured lines).

The advantages of this method of photopolymerisation are:

- (i) After exposure the initiation and propagation of cationic polymerisation may continue in the dark.
- (ii) Cationic polymerisation is not inhibited by atmospheric oxygen.

A series of patents has covered the use of diazonium salts<sup>79</sup> for polymerisation of epoxy systems (for example, epichlorhydrin-bisphenol-A prepolymers). Improved dark storage stability of formulations has been claimed with addition of substituted ureas<sup>80</sup>, sulfoxides<sup>81</sup>, nitriles<sup>82</sup>, or cyclic amides<sup>83</sup>.

Later patents claim the use of epoxides in blends with lactones or vinyl containing compounds<sup>84</sup>, and less than 5 per cent of aryl diazo salt is required even in pigmented systems. Preferred salts include those of 2,5-dimethoxy, 4-tolyl-thio, benzene diazo, and the diethoxy compound:



### Other photosensitisers

Refs. 86-96

The main groups of photosensitisers not covered above include:

- (i) Halogenated hydrocarbons<sup>86</sup>, for example, polychlorinated di- and triphenyls.
- (ii) Other halogenated compounds<sup>87</sup>, for example, substituted chloracetophenones, and sulfonyl chlorides.
- (iii) Acetophenone derivatives<sup>88</sup>.
- (iv) Benzophenone derivatives<sup>89</sup>, mixtures of benzophenone and Michler's ketone are particularly effective, but large additions are necessary, typically 10-15 per cent on resin.
- (v) Heterocyclics, for example, acridine or phenazine types<sup>90</sup>.
- (vi) Metallocenes<sup>91</sup>.
- (vii) Sulfur compounds<sup>92</sup>, such as dioxanthenes, thioxanthenes and aromatic disulfides.
- (viii) Polycyclic quinones<sup>93</sup>.
- (ix) Dyestuff—redox systems<sup>94</sup>.

UV-photopolymerisable systems have been the subject of patents in diverse fields, including: printing inks and plates; paints and lacquers, including insulating lacquers<sup>95</sup>; grain fillers for wood board; dental coatings; surgical casts<sup>96</sup>; adhesives; transfer-printing of textiles; printed circuits. The unique capabilities of UV-curable compositions assure their future development for many other end uses.

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# Photopolymerisation: the kinetics of a-type photopolymerisation\*

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## Summary

The concept of "photopolymerisation" is discussed and illustrated with several examples; the validity of the reaction scheme is proved for the photopolymerisation of substituted N,N'-alkylene bismaleimides.

A kinetic analysis of the photopolymerisation of a bichromophoric system A-A, where the two chromophores react independently, is presented. The photochemical reaction can occur either at the first

excited singlet state or at the triplet excited state or at both excited states of the chromophore.

A generalised Stern-Volmer equation is derived for the quenching of product formation by a quencher which deactivates both excited singlet and triplet states of the reactant. This equation is discussed with reference to various limiting cases.

## Keywords

*Processes and methods primarily associated with:*

*manufacturing or synthesis*

*photoinitiation*

*drying or curing of coatings*

*photoinitiation  
photopolymerisation  
ultraviolet curing*

## Photopolymérisation: la cinétique de photopolymérisation du type 'a'

### Résumé

On discute le concept de "photopolymérisation" et on l'éclaire au moyen de divers exemples. On démontre la validité du schéma de réaction dans le cas de la photopolymérisation des bismaléimides d'alkylènes N,N'-substitués.

On présente une analyse cinétique de la photopolymérisation des systèmes bichromophoriques du type A-A, où les deux groupes chromophores réagissent indépendamment de l'autre. La réaction

photochimique peut se produire soit pendant le premier état excité du singlet, soit à l'état excité du triplet, soit à tous les deux états excités du groupe chromophore.

On dérive une équation généralisée du type Stern-Volmer pour décrire l'extinction de la réaction effectuée par un extincteur qui désactive à la fois les états excités du singlet et du triplet. On discute cette équation à l'égard des cas limites.

## Photopolymerisation: die Kinetik der a-Typ Photopolymerisation

### Zusammenfassung:

Eine Besprechung des anhand verschiedener Beispiele erläuterten Konzeptes der "Photopolymerisation"; die Gültigkeit des Reaktionsschemas für die Photopolymerisation von substituierten N,N'-Alkylenbismaleimiden wird bewiesen.

Eine kinetische Analyse der Photopolymerisation eines bichromophoren Systems A-A, in welchem die beiden Chromophoren unabhängig reagieren, wird beschrieben. Die photochemische Reaktion kann entweder im ersten sensibilisierten Singlet-Stadium

oder im sensibilisierten Triplet-Stadium oder in beiden sensibilisierten Stadien des Chromophors vor sich gehen.

Eine verallgemeinerte Stern-Volmer Gleichung wird abgeleitet für Auslöschung einer Produktbildung durch einen "Quencher", welcher beide sensibilisierten Singlet- und Tripletstadien des Ausgangsstoffes deaktiviert. Diese Gleichung wird mit Bezug auf Grenzfälle besprochen.

## Introduction

*Refs. 1-12*

The term "photopolymerisation" has recently been defined<sup>1-4</sup> as:

*a polymerisation process in which every chain-propagating step involves a photochemical reaction.*

From this statement, it follows that photopolymerisation should be considered a multi-step reaction, in contrast to photoinitiated polymerisation, which is a chain process.

Photopolymerisation can, in principle, be divided into two classes:

- (i) Type *a* photopolymerisation, in which propagation occurs by the reaction of a molecule in an excited state with another in the ground state.
- (ii) Type *b* photopolymerisation, in which propagation occurs by the reaction of a reactive ground-state species, formed earlier by a photochemical reaction (for example, radical re-combination).

The type *a* photopolymerisation can be subdivided further into singlet and triplet photopolymerisation, depending on the nature of the excited state involved in the propagation step. An example of each of these has been reported: the photopolymerisation of bisanthracenes<sup>5</sup> exemplifies the singlet photopolymerisation, whilst the photopolymerisation of

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substituted N,N'-alkylene bismaleimides<sup>1,3,6,7</sup> occurs via the triplet excited state.

Solid-state photopolymerisation can be regarded as a special case of *a*-type photopolymerisation.

An extensive study of this lattice controlled photopolymerisation has been made by Hasegawa and co-workers<sup>8</sup>, and has recently been extended to include the synthesis of optically active polymers<sup>9</sup>.

The type *b* photopolymerisation can also be subdivided into two classes: one in which the reactive ground state is formed by a monomolecular process, for example the photopolymerisation of bisazides<sup>10</sup>, and the other in which the formation of the reactive ground state involves a bimolecular reaction, for example the photopolymerisation of bisbenzophenones<sup>11</sup>.

This concept is not restricted to homopolymerisation, but can readily be extended to copolymerisation. Although the number of reports in this field is still limited<sup>12</sup>, there are a number of quite interesting theoretical and practical possibilities. It is, indeed, possible to have two co-monomers with identical photochemical properties, but with different structures, leading to purely statistical copolymers ( $r_1=r_2=1$ ). Since the photopolymers are "living polymers", it can be easily seen that block copolymers could be obtained. By choosing the system correctly, it would further be possible to develop systems which would lead to purely alternating copolymers.

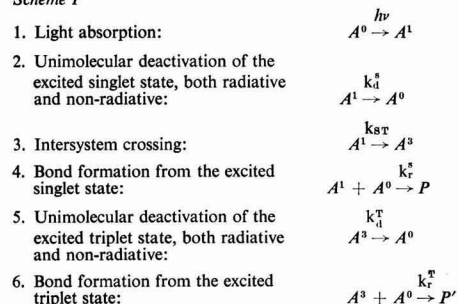
Another interesting point is the reversibility of many photochemical reactions. This property could be used not only in photodegradations, but eventually in the re-use of certain materials.

In order to demonstrate that the definition of photopolymerisation given here is not just a question of semantics, a general kinetic analysis of *a*-type photopolymerisation is presented.

### Kinetic scheme and kinetic equations

The general kinetic reaction scheme for the photopolymerisation of a bichromophoric system *A-A*, where the two chromophores react independently is considered. The photochemical reaction can occur either from the first excited singlet state (*A*<sup>1</sup>) or from the triplet excited state (*A*<sup>3</sup>) or from both excited states of the chromophore *A*. The probability of simultaneous excitation by conventional

#### Scheme I



continuous light sources of two chromophores of the bichromophoric system is negligible. The photopolymerisation reaction can, therefore, be described by scheme I below where *A*<sup>0</sup> represents the chromophore in its ground state.

In this scheme, it is assumed that each excited state can yield a photocyclo-addition product with a configuration different from any of the others and that every process is irreversible. The overall reaction rate for the disappearance of the chromophore *A*<sup>0</sup>, is given by equation (1).

$$-d[A^0]/dt = I_{abs} + k_r^s[A^1][A^0] + k_r^t[A^3][A^0] - k_d^s[A^1] - k_d^t[A^3] \dots \dots \dots (1)$$

where [ ] represents molar concentration and *I*<sub>abs</sub> the absorbed light intensity in einstein l<sup>-1</sup>s<sup>-1</sup>.

Steady state analysis in excited singlet states leads to equation (2).

$$[A^1] = \frac{I_{abs}}{k_d^s + k_{ST} + k_r^s[A^0]} \dots \dots \dots (2)$$

Similarly for triplet states:

$$k_{ST}[A^1] = [A^3](k_d^t + k_r^t[A^0]) \dots \dots \dots (3)$$

Substituting equation (2) into (3) gives:

$$[A^3] = \frac{I_{abs} k_{ST}}{(k_d^t + k_r^t[A^0])(k_d^s + k_{ST} + k_r^s[A^0])} \dots \dots \dots (4)$$

Equation (1) can then be rearranged to give:

$$-\frac{d[A^0]}{dt} = \frac{2 I_{abs} [A^0]}{k_d^s + k_{ST} + k_r^s[A^0]} \left( k_r^s + \frac{k_r^t k_{ST}}{k_d^t + k_r^t[A^0]} \right) \dots \dots (5)$$

#### Photopolymerisation involving the excited singlet state

In this case, the bimolecular photochemical reaction proceeds only via the excited singlet state.

This means that  $k_r^t = 0$  and equation (5) simplifies to:

$$-\frac{d[A^0]}{dt} = \frac{2 I_{abs} k_p^s [A^0]}{k_d^s + k_{ST} + k_r^s [A^0]} \dots \dots \dots (6)$$

#### Total absorption

If all the incident light is absorbed by the system, then *I*<sub>abs</sub> = *I*<sub>0</sub>, where *I*<sub>0</sub> is the intensity of light with a given wavelength incident per unit of time on to the front of the system.

Integration of equation (6) between the time limits *t* and *t*<sub>0</sub>, when the concentrations are [*A*<sup>0</sup>]<sub>0</sub>(1-*p*) and [*A*<sup>0</sup>]<sub>0</sub> respectively gives:

$$2.303 \frac{k_d^s + k_{ST}}{k_r^s [A^0]_0} \log \left( \frac{1}{1-p} \right) + p = \frac{2I_0(t-t_0)}{[A^0]_0} \dots \dots \dots (7)$$

where [*A*<sup>0</sup>]<sub>0</sub> is the chromophore concentration in the ground state at time *t*<sub>0</sub> and *p* is the degree of conversion at time *t*.

#### Very little absorption

If the system absorbs only a small fraction of the incident light, then *I*<sub>abs</sub> = *I*<sub>0</sub>α*L*[*A*<sup>0</sup>], where α is the absorption coefficient for the chromophore *A* at the wavelength, equal to 2.303 times the molar absorption coefficient ε, of the chromophore, and *L* stands for the light path (in cm).

Integration of equation (6) within the same limits as mentioned in the previous section and with  $I_{\text{abs}} = 2.303 \epsilon L I_0 [A^0]$ , gives:

$$\left( \frac{k_d^s + k_{ST}}{2.303 k_r^s [A^0]_0} \right) \left( \frac{p}{1-p} \right) + \log \left( \frac{1}{1-p} \right) = 2I_0 \epsilon L (t-t_0) \dots (8)$$

**Partial absorption**

In the intermediary case,  $I_{\text{abs}}$  given:

$$I_{\text{abs}} = I_0 \left( \alpha [A^0] L - \frac{\alpha^2 [A^0]^2 L^2}{2!} + \frac{\alpha^3 [A^0]^3 L^3}{3!} - \dots \right) \dots (9)$$

A more complicated kinetic equation is obtained after substituting equation (9) into equation (6) and integrating (6) between the same limits as for the case of total absorption.

**Photopolymerisation involving the first excited triplet state**

When  $k_r^s$  equals zero, equation (5) simplifies to:

$$-\frac{d[A^0]}{dt} = \frac{2I_{\text{abs}} \Phi_{\text{disc}} k_r^T [A^0]}{k_d^T + k_r^T [A^0]} \dots (10)$$

where  $\Phi_{\text{disc}} = \frac{k_{ST}}{k_d^s + k_{ST}} \dots (11)$

which equals the quantum yield for intersystem crossing in the absence of a reaction.

**Total absorption**

If all the incident light energy is absorbed by the system, integration of equation (10), between the same limits as in the case of total absorption for the singlet state, gives:

$$\frac{2.303 k_d^T}{k_r^T [A^0]_0} \log \left( \frac{1}{1-p} \right) + p = \frac{2 I_0 \Phi_{\text{disc}} (t-t_0)}{[A^0]_0} \dots (12)$$

**Very little absorption**

If the system absorbs only a small fraction of the incident light, then equation (10), upon integration between the same limits as above, will give:

$$\frac{k_d^T}{2.303 k_r^T [A^0]_0} \left( \frac{p}{1-p} \right) + \log \left( \frac{1}{1-p} \right) = 2 \Phi_{\text{disc}} I_0 \epsilon L (t-t_0) \dots (13)$$

**Partial absorption**

In the intermediate cases, a more complicated equation is obtained.

**Photopolymerisation involving the first excited singlet and the first excited triplet states**

**Total absorption**

If all the incident light is absorbed by the system, equation (5) can be integrated between the same limits as above, and this gives:

$$\frac{2.303 K}{M[A^0]_0} \log \frac{1}{1-p} + p + \frac{2.303 (LM-KN)}{MN[A^0]_0} \log \left( \frac{M+N[A^0]_0}{M+N[A^0]_0(1-p)} \right) = \frac{2 I_0 (t-t_0)}{[A^0]_0} \dots (14)$$

where  $K = k_d^T (k_d^s + k_{ST})$

$L = k_d^s k_r^T$

$M = k_r^s k_d^T + k_r^T k_{ST}$

$N = k_r^s k_r^T$

**Very little absorption**

If only a small fraction of the incident light is absorbed, then integration of equation (5) between the same limits as mentioned above will give:

$$\frac{K}{2.303 M [A^0]_0} \left( \frac{p}{1-p} \right) + \log \left( \frac{1}{1-p} \right) + \frac{LM-KN}{M^2} \log \left( \frac{M+N [A^0]_0 (1-p)}{(M+N [A^0]_0) (1-p)} \right) = 2 I_0 \epsilon L (t-t_0) \dots (15)$$

**General remarks**

Refs. 3, 4, 6, 8, 14

For symmetrical bichromophoric compounds (type A-A), where the chromophores do not react independently, the kinetic scheme presented above is not valid.

For symmetrical bichromophoric systems (type A-A), where the chromophores react independently, the reactivity of the chromophores is independent of the link between the two chromophores. In this case, the concentration of chromophore A in the ground state, which can be determined spectroscopically, is twice the concentration of the bichromophoric system A-A in the ground state. It has been shown experimentally<sup>3,4,6</sup> that in these photopolymerisations,  $\bar{x}_n = 1/(1-p)$  as in a multi-step polymerisation:  $\bar{x}_n$  is the degree of polymerisation. The equations (7), (8), (12)-(15) can be expressed in terms of the "degree of polymerisation".

From the ratio of rates of product formation from the singlet and triplet excited states, the following equation can be derived:

$$\frac{dP}{dP'} = \frac{k_r^s}{k_{ST}} \left( \frac{k_d^T}{k_r^T} + [A^0] \right) \dots (16)$$

If  $dP/dP'$  can be measured, a plot of  $dP/dP'$  as a function of  $[A^0]$  will give a straight line with slope  $k_r^s/k_{ST}$  and intercept  $(k_r^s/k_{ST}) \times (k_d^T/k_r^T)$ .

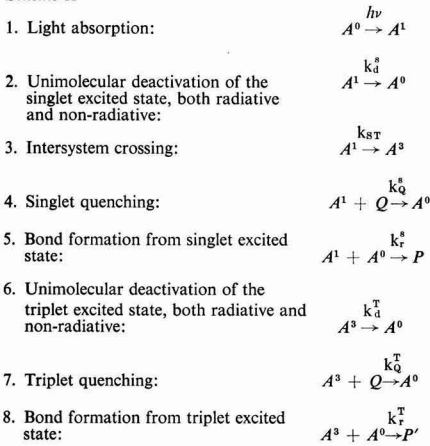
**Photopolymerisation involving quenching of both singlet and triplet excited states**

Refs. 7, 8

The bimolecular reaction, which can occur from both the excited singlet state ( $A^1$ ) and excited triplet state ( $A^3$ ) will be considered.

This photopolymerisation is described by scheme II, where the added quencher Q is assumed to quench both excited singlet and triplet states of A. It is also assumed that the inter-system crossing from the excited singlet to triplet state is irreversible.

Scheme II



The total quantum yield for the disappearance of the chromophore in the photochemical bimolecular reaction in the presence of quencher  $\Phi_r$  (equation 17) will equal the sum of the quantum yields for reaction from the singlet  $\Phi_r^s$  and triplet  $\Phi_r^t$  states (equations 18 and 19).

$$\Phi_r = \Phi_r^s + \Phi_r^t \dots\dots\dots(17)$$

$$\Phi_r^s = \frac{2 k_r^s [A^0]}{k_r^s [A^0] + k_d^s + k_{ST} + k_Q^s [Q]} \dots\dots\dots(18)$$

$$\Phi_r^t = \frac{2 k_{ST}}{k_{ST} + k_d^s + k_r^s [A^0] + k_Q^s [Q]} \times \frac{k_r^t [A^0]}{k_r^t [A^0] + k_d^t + k_Q^t [Q]} \dots\dots\dots(19)$$

Then  $\Phi_r$  can be expressed by:

$$\Phi_r = \frac{2 [A^0]}{k_d^s + k_{ST} + k_r^s [A^0] + k_Q^s [Q]} \times \left( \frac{k_r^s (k_r^t [A^0] + k_d^t + k_Q^t [Q]) + k_{ST} k_r^t}{k_d^t + k_r^t [A^0] + k_Q^t [Q]} \right) \dots\dots\dots(20)$$

If  $[Q]$  equals zero in equation (20), the total quantum yield for the reaction in the absence of quencher  $\Phi_r^0$  is obtained thus:

$$\Phi_r^0 = \frac{2 [A^0]}{k_d^s + k_{ST} + k_r^s [A^0]} \left( \frac{k_r^s (k_r^t [A^0] + k_d^t) + k_{ST} k_r^t}{k_d^t + k_r^t [A^0]} \right) \dots\dots\dots(21)$$

Division of equation (21) by (20) yields  $\Phi_r^0/\Phi_r$ , the Stern-Volmer relationship:

$$\frac{\Phi_r^0}{\Phi_r} = \left( 1 + \frac{k_Q^s [Q]}{k_d^s + k_{ST} + k_r^s [A^0]} \right) \left( 1 + \frac{k_Q^t [Q]}{k_d^t + k_r^t [A^0]} \right) \times \left( \frac{1 + k_{ST} k_r^t / k_r^s (k_r^t [A^0] + k_d^t)}{1 + [k_Q^s [Q] / (k_r^t [A^0] + k_d^t)] + k_{ST} k_r^t / k_r^s (k_r^t [A^0] + k_d^t)} \right) \dots\dots\dots(22)$$

If  $[Q]$  is set equal to zero in equations (18) and (19), the quantum yields for singlet ( $\Phi_r^{s0}$ ) and triplet ( $\Phi_r^{t0}$ ) reactions

in the absence of quencher are expressed by equations (23) and (24); the ratio  $(\Phi_r^{t0})/(\Phi_r^{s0})$  is given in equation (25).

$$\Phi_r^{s0} = \frac{2 k_r^s [A^0]}{k_r^s [A^0] + k_d^s + k_{ST}} \dots\dots\dots(23)$$

$$\Phi_r^{t0} = \frac{2 k_{ST}}{k_{ST} + k_d^s + k_r^s [A^0]} \times \frac{k_r^t [A^0]}{k_d^t + k_r^t [A^0]} \dots\dots\dots(24)$$

$$\frac{\Phi_r^{t0}}{\Phi_r^{s0}} = \frac{k_r^t k_{ST}}{k_r^s (k_d^t + k_r^t [A^0])} \dots\dots\dots(25)$$

The singlet  $\tau_s^0$  and triplet  $\tau_t^0$  lifetimes of  $A$  in the absence of quencher are given by equations (26) and (27).

$$\tau_s^0 = \frac{1}{k_d^s + k_{ST} + k_r^s [A^0]} \dots\dots\dots(26)$$

$$\tau_t^0 = \frac{1}{k_d^t + k_r^t [A^0]} \dots\dots\dots(27)$$

Substitution of these expressions into equation (22) yields a generalised Stern-Volmer expression for bimolecular photochemical reaction, involving both reaction and quenching from both excited singlet and triplet states:

$$\frac{\Phi_r^0}{\Phi_r} = (1 + k_Q^s [Q] \tau_s^0) (1 + k_Q^t [Q] \tau_t^0) \times \left( \frac{1 + (\Phi_r^{t0} / \Phi_r^{s0})}{1 + (\Phi_r^{t0} / \Phi_r^{s0}) + k_Q^s [Q] \tau_s^0} \right) \dots\dots\dots(28)$$

This expression for the Stern-Volmer plot is analogous to the equation obtained by Dalton and Turro<sup>7</sup> for the unimolecular photochemical re-arrangement, which occurs from both the first excited singlet and the first excited triplet states of the reactant. It should be pointed out that the terms  $\tau_s^0$ ,  $\tau_t^0$  and  $\Phi_r^{t0}/\Phi_r^{s0}$  will involve the changing concentration of the chromophore  $A$  with time. In quenching experiments, the change in concentration of  $A^0$  is usually small, so that  $[A^0]$  may be replaced by  $[A^0]_0$ , the initial chromophore concentration. In this case  $\tau_s^0$ ,  $\tau_t^0$  and the ratio  $\Phi_r^{t0}/\Phi_r^{s0}$  become constants.

The initial slope of the Stern-Volmer plot is given by the derivative of equation (28) with respect to  $[Q]$  as  $[Q] \rightarrow 0$ , thus:

$$k_Q^s \tau_s^0 \left( 1 + \frac{\Phi_r^{t0}}{\Phi_r^{s0}} \right) - \frac{(\Phi_r^{t0} / \Phi_r^{s0}) [k_Q^s \tau_s^0 (1 + \Phi_r^{t0} / \Phi_r^{s0}) - k_Q^t \tau_t^0]}{1 + \Phi_r^{t0} / \Phi_r^{s0}} \dots\dots\dots(29)$$

The final slope (of the asymptote) of the Stern-Volmer plot is given by the derivative of equation (28) with respect to  $[Q]$  as  $[Q] \rightarrow \infty$ , thus:

$$\text{Final (asymptotic) slope} = k_Q^s \tau_s^0 [1 + \Phi_r^{t0} / \Phi_r^{s0}] \dots\dots\dots(30)$$

It is now possible to examine the behaviour of equation (28) as a function of the values  $\Phi_r^{t0}/\Phi_r^{s0}$ ,  $k_Q^s \tau_s^0$ ,  $k_Q^t \tau_t^0$ , which can all be considered constants if the extent of reaction is small.

From inspection of equations (29) and (30), the following conclusions can be drawn:

Stern-Volmer plots, in cases where both reaction and quenching can occur from both the first excited singlet and triplet states, may curve downward and approach a straight line at large  $[Q]$  values, with lower slope than the initial slope, when  $k_Q^s \tau_s^0 [1 + (\Phi_r^{t0} / \Phi_r^{s0})] < k_Q^t \tau_t^0$ ;

or curve upward and asymptotically approach a straight line, with a higher slope than the initial slope, when  $k_q^s \tau_s^0 [1 + (\Phi_r^{0T}/\Phi_r^{0S})] > k_q^T \tau_r^0$

or remain linear when  $k_q^s \tau_s^0 [1 + (\Phi_r^{0T}/\Phi_r^{0S})] = k_q^T \tau_r^0$ .

Under the last of these conditions, the expression for the Stern-Volmer equation (28) becomes equivalent to:

$$\frac{\Phi_r^0}{\Phi_r} = 1 + k_q^T [Q] \tau_r^0 = 1 + k_q^s \tau_s^0 [1 + (\Phi_r^{0T}/\Phi_r^{0S})] [Q] \dots (31)$$

which means that the Stern-Volmer plot and the oblique asymptote can be regarded as identical straight lines. It should be pointed out that linear Stern-Volmer plots do not necessarily imply simple kinetics with regard to reaction rate and quenching from just one excited state<sup>8</sup>.

A linear Stern-Volmer plot will then be obtained for a chromophore concentration  $[A^0]$  given by:

$$[A^0] = \frac{k_q^T k_r^s (k_d^s + k_{ST}) - k_q^s (k_d^T k_r^s + k_r^T k_{ST})}{k_r^s (k_r^T k_q^s - k_q^T k_r^s)} \dots (32)$$

If  $k_r^T k_q^s = k_q^T k_r^s$  and  $k_q^s k_r^T = k_r^T k_q^s$  a linear Stern-Volmer plot will be obtained for all chromophore concentrations. Again it should be stressed that a linear Stern-Volmer plot does not necessarily imply a simple kinetic reaction scheme<sup>14</sup>.

**Two excited states quenched, only one reactive**

*Singlet state reactive*

When only the singlet excited state is reactive and the two excited states are quenched, the term  $k_r^T$  becomes equal to zero and equation (28) simplifies to:

$$\frac{\Phi_r^0}{\Phi_r} = 1 + \frac{k_q^s [Q]}{k_d^s + k_{ST} + k_r^s [A^0]} \dots (33)$$

A plot of  $\Phi_r^0/\Phi_r$  as a function of  $[Q]$  will give a straight line with a slope  $k_q^s \tau_s^0$ . If the rate constant  $k_q^s$  is assumed to be diffusion controlled,  $\tau_s^0$  can be calculated and a plot of  $1/\tau_s^0$  as a function of  $[A^0]$  will yield  $k_d^s + k_{ST}$  and  $k_r^s$ .

*Triplet state reactive*

In this case,  $k_r^s$  becomes zero and the last term in equation (28) becomes equal to unity, giving the Stern-Volmer expression:

$$\frac{\Phi_r^0}{\Phi_r} = \left( 1 + \frac{k_q^s [Q]}{k_d^s + k_{ST}} \right) \left( 1 + \frac{k_q^T [Q]}{k_d^T + k_r^T [A^0]} \right) \dots (34)$$

This represents a quadratic equation and thus has no oblique asymptote.

**Two excited states reactive, only one quenched**

*Singlet state quenched*

In this case,  $k_q^T$  becomes zero and the Stern-Volmer expression is re-arranged to equation (33).

*Triplet state quenched*

In this situation,  $k_q^S$  is reduced to zero and equation (28) simplifies to:

$$\frac{\Phi_r^0}{\Phi_r} = (1 + k_q^T [Q] \tau_r^0) \left( \frac{1 + (\Phi_r^{0T}/\Phi_r^{0S})}{1 + (\Phi_r^{0T}/\Phi_r^{0S}) + k_q^T [Q] \tau_r^0} \right) \dots (35)$$

so that the initial slope IS is given by:

$$IS = \frac{k_q^T \tau_r^0 \Phi_r^{0T}}{\Phi_r^{0S} + \Phi_r^{0T}} \dots (36)$$

This curve approaches a horizontal asymptote given by  $(1 + \Phi_r^{0T}/\Phi_r^{0S})$ .

**One excited state quenched, the other reactive**

*Singlet state reacts, triplet state quenched*

In this extreme case,  $k_q^S = 0$ ,  $k_r^T = 0$  and  $(\Phi_r^0/\Phi_r)$  equals unity for all values of  $[Q]$ .

*Triplet state reacts, singlet state quenched*

In this other extreme case,  $k_q^T = 0$ ,  $k_r^S = 0$  and equation (28) simplifies to:

$$\frac{\Phi_r^0}{\Phi_r} = 1 + \frac{k_q^s [Q]}{k_d^s + k_{ST}} \dots (37)$$

The Stern-Volmer plot of  $\Phi_r^0/\Phi_r$  versus  $[Q]$  will be linear. If  $k_q^s$  is diffusion controlled,  $(k_d^s + k_{ST})$  can be evaluated. It should be noted that in this case, the measured lifetime is independent of  $[A^0]$ .

**One excited state is reactive and is quenched**

*Singlet*

In this case, equation (33) is obtained by the substitution  $k_r^T = k_q^T = 0$ .

*Triplet*

Substitution of  $k_r^S = k_q^S = 0$  in equation (28) and re-arrangement gives:

$$\frac{\Phi_r^0}{\Phi_r} = 1 + \frac{k_q^T [Q]}{k_d^T + k_r^T [A^0]} \dots (38)$$

A plot of  $\Phi_r^0/\Phi_r$  as a function of  $[Q]$  gives a straight line with a slope  $k_q^T \tau_r^0$ . If  $k_q^T$  is diffusion controlled,  $k_d^T$  and  $k_r^T$  can be calculated.

**Validity**

Refs. 6, 7

The validity of the proposed kinetic scheme was recently proved<sup>6,7</sup> in the photopolymerisation of substituted N,N'-alkylene bismaleimides. The rate constants and quantum yields obtained for the photopolymerisation were, within the limits of experimental error, identical with those obtained from the model systems.

### Acknowledgment

Mr N. Boens is indebted to the Nationaal Fonds voor Wetenschappelijk Onderzoek for a fellowship.

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## Next month's issue

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

**Determination of the colorimetric values of colours to BS 381C** by R. J. Hancox and L. A. Hill

**Some aspects of the formulation of UV-curable polyester based systems** by A. Laws, S. Lynn and R. Hall

**The use of polyfunctional monomers in UV curing** by J. R. Younger

**Sensitisation and stabilisation in monomer/polymer systems** by D. Phillips

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*The papers in this issue were first presented at a Symposium of the Newcastle Section, entitled "Ultraviolet polymerisation", held at Durham University on 10 and 11 April 1975. Other papers from the Symposium will be published in the Journal during the next few months. The Association is preparing a limited number of reprints of these papers to be collated and bound as a separate volume and offered for sale. It is expected that the book will be available in the summer of 1976, and further information regarding availability will be published in the Journal in due course.*

May 1976



# Bristol

### Modern techniques of wood preservation

The Chairman, Mr L. J. Brooke, introduced the lecturer Mr R. E. Hambling, Technical Manager of Cuprinol Ltd. Mr Hambling described three main types of wood preservation: water-borne inorganic types; creosote, by vacuum and pressure application; and the organo-metallic types, applied as solutions in hydrocarbon solvents.

The use of these preservatives in the joinery business was discussed and, in particular, attention drawn to the differing requirements dependent upon the size of the joinery operation, especially with regard to application techniques. Before 1960 there was little demand for the preservation of wood used in joinery and most of the developments had taken place in the last 10 years. Methods of impregnation of the preservatives were described, especially those which gave optimum preservation, minimum disruption of joinery production and no adverse effect on finishing systems.

The paper was well received, and the question period was opened by Mr M. A. Lageu and the vote of thanks to the lecturer proposed by Mr G. W. Fawkes.

J.R.T.

### Photopolymer printing plates

A lecture was given on 27 February 1976 by Mr E. Eccles of BASF (United Kingdom) Ltd on photopolymer printing plates, with Mr L. J. Brooke in the Chair.

The lecturer began by showing a film describing the "Nyloprint process" which has been developed by BASF and which was suitable for letterpress printing: the plate in this process consists of a photosensitive nylon layer bonded to a backing material, which can be rigid or flexible. Exposure to UV light causes photopolymerisation, which renders the exposed portions insoluble and so forms the print in relief. The advantages of this process were described.

The questioning of the lecturer was opened by Mr J. R. Taylor and an interesting discussion by Members present ensued.

J.R.T.

# London

### Ontario Branch

#### Colour in advertising

At a meeting held on 10 March 1976 at the Skyline Hotel, Toronto, Mr N. Speke, Art Director of McKim Advertising, gave a talk on "Colour in advertising". He pointed out that his paper was necessarily non-technical as the application of colour in this sphere followed no hard and fast rules. There were, however, certain "givens" which were dictated by common sense, past experience and intuition. Thus, the style in advertising was dictated by the desired image, the form by the function, the content by the nature of the product, and the tone by the desired mood.

By association, colour could be related to other qualities, such as touch, sound, taste, odour and shape. For example, red was associated with heat, with the sound of a bugle, high food appeal, square or cubic structures, and was physically stimulating. Blue was associated with cold, with the strings of an orchestra, poor food appeal, spherical shapes, and was physically soothing. Orange represented the brass section of an orchestra, high food appeal, rectangular shapes, conviviality and friendliness. Yellow was associated with freshness, with flutes, pipes and pyramids, and denoted a healthy and sunny

disposition. Green could be associated with garden freshness but also with spoilage, and physically promoted healing and had a soothing or sedative effect; in fact, it was used in the treatment of exhaustion.

Odours were more associated with shades than with tones; light colours with light odours, and strong colours with strong odours.

The precise use of colour in cartoons leads to dramatic effects, whilst in posters judicious use of colour was necessary.

The colour "sepia" was used to give traditional effects of old-fashioned goodness. The fact that colours had gained certain associations throughout the years was shown in many idiomatic expressions: seeing red—red letter days—jaundiced views—greenhorn—green with envy—feeling blue—black despair. Even today, new expressions were becoming familiar, such as "blue movies".

The use of colour in advertising was an attempt to communicate by association, and the success (or otherwise) of this was evident only after exposure to the public; of thousands of such exposures, only some stood out and illustrated the effectiveness of good colour selection.

The talk ended with descriptions of typical examples of good advertising, which were graphically illustrated by excellent slides. A total of 45 Members and guests attended the meeting in spite of the inclement weather. The vote of thanks to Mr Speke was proposed by Mr A. Chassels.

H.L.

# Scottish

### The coating technologist in a changing world

A meeting was held in the Beacons Hotel, Glasgow at 6.00 p.m. on 11 March 1976. Mr A. McLean introduced the President, Mr A. T. S. Rudram, to talk on "The coating technologist in a changing world".

In his opening remarks, Mr Rudram gave his definition of the coating technologist as someone with an aptitude for using products and information, rather than as someone who was an innovator.

Two major political changes had affected the industry over the last two to three decades:

- (a) the emergence and impact of the so-called "third world" countries, and
- (b) formation and enlargement of the EEC.

In the third world areas, production plants had been initiated, controlled and staffed by UK personnel. Now these sites were also served by local, fully qualified technologists and this would be an increasing trend as local colleges and universities supplied trained personnel. Dealings between UK headquarters and overseas interests on matters affecting the latter were best optimised if there existed a thorough understanding of local habits, ways of life and pressures. Mr Rudram felt that, in general, local staffing had led to an improvement in total efficiency.

To date, the major influence of the EEC had been on regulations, especially on safety and environmental matters. Although this could involve prolonged argument, the coating industry was given a fair voice and regulations were and would continue to be reasonable. The coating technologist's life would, however, become more complex; the EEC issue had indicated how essential it was properly to record and analyse information.

Looking for future trends was extremely difficult, but Mr Rudram felt that the coating industry would be influenced by the OPEC control of petroleum sources and this might lead to a greater use of (vegetable) raw materials, which could be regenerated. This would be influenced by the "green revolution", which itself would require greater environmental control to optimise agrarian output.

A wide ranging discussion followed, with the environmental and health regulation being debated fully. It was recognised by Mr Rudram that regulations varied throughout the world and within Europe and, as such, could allow manufacture and use in certain areas more easily than in others. He recognised that there could be an argument of quality versus restrictions, but felt that this was not all that evident in reality. Certainly, effects on health and environment was rapidly becoming a more important criterion of quality.

Mr R. Morrow proposed a vote of thanks and all those present expressed their appreciation in the usual way.

G.H.R.

## South African

### Transvaal Branch

#### Emulsion-based paints for wood

Mr O. Vorster of the National Building Research Institute lectured to a meeting held at the Boulevard Hotel, Pretoria on Thursday 19 February 1976.

Among the more recently introduced paints for buildings in South Africa were wood primers and paints based on polymer emulsion vehicles.

The durability characteristics of a number of emulsion-based primers had been examined on South African pine at three different exposure locations, namely Pretoria, Durban and Cape Town. A marked difference was noticed in results obtained at these three sites.

The most durable primer was found to be a 30 per cent PVC/acrylic emulsion and next best was a 40 per cent PVC/acrylic emulsion, modified with a long oil alkyd. The other binders included in this investigation were PVAc/maleate co-polymer and "Veova" emulsions.

The most successful top-coats with the above mentioned primers were based on acrylic and PVAc/maleate co-polymer emulsions.

P.A.J.G.

## Wellington

### Hazardous materials

The Section held a half-day symposium entitled "Hazardous materials—handling and identification" on Tuesday 26 August 1975 at Industry House, Wellington.

OCCA combined with the New Zealand Paint Manufacturers' Association in organising the symposium with a panel of four speakers: Mr E. G. Thompson, Secretary of Federation of Labour; Mr G. Hodson, ICI (NZ) Ltd; Mr S. Thomas, Fire Services Commission; Mr I. McDonald, Government Analyst. Mr T. Slinn of Dulux New Zealand Ltd chaired the session.

A hundred delegates attended, with representatives from importing companies, shipping companies, drivers, watersiders, and storemen packers' unions and scientists. Government bodies represented were: Police Department, the Inspector of Explosives and Fire Services.

Mr Thompson commenced by saying that the FOL saw the major factor contributing to accidents involving dangerous

chemicals as a poor understanding of the potential hazards. Vast improvements were needed in safety provisions, regulations and codes, and education was essential in regard to the handling of chemicals.

Mr Hodson said that importers must bear some responsibility for accidents. He added that New Zealand has access to more markets than almost any other country in the world, which compounded the problems.

Another problem was that end-users asked importers to code drums of hazardous chemicals for patent or security reasons and, therefore, the end-user should also bear a responsibility.

A recent cause of incidents was the shortages of raw materials, which had forced importers to take whatever they could obtain and which had resulted in some chemicals being poorly or inadequately packed with resulting spillages. Poor documentation was another problem.

Mr Thomas appealed for common sense, stating that the fire service would seek legislation only if common sense did not prevail.

After the agricultural chemical spillage at Auckland in 1973, incidents reported to the fire services had increased dramatically. He appealed for a form of labelling that could give firemen warning from a distance when confronted with a spillage or accident.

Proper securing of drums was required during transport. Transport regulations required loads to be "reasonably secure", but did not take into account vehicle accidents or sudden braking. Truck drivers should be told what they were carrying, and whether the chemical would be safe to approach after a spillage.

Mr McDonald said there was an obvious need for a dangerous goods centre in New Zealand. A universal labelling system was desirable, classifying chemicals into groups, for example, "corrosive", "flammable", "poisonous", etc.

Mr T. Slinn, chairman of the symposium, strongly urged industry to consider dealing with a single body, and not a variety of organisations as at present.

Four recommendations were passed at the end of the four-hour meeting:

1. That the symposium suggest to the Minister of Internal Affairs and Transport that consideration be given to insistence that chemical raw materials be adequately described, labelled and packaged with regard to their hazardous or toxic nature at their point of origin, and documentation be transferred to New Zealand.
2. That it be recommended to the interdepartmental committee (currently looking at the problem) that the aims of the present review of the handling and transportation of hazardous materials should importantly and necessarily include the co-ordination of all statutory and regulatory requirements in the hands of one administrative authority and to bring into force one code and specification (or text book) covering all regulatory requirements including identification and labelling systems.
3. That the paint manufacturers as an industry and, where appropriate, members of the Association should attempt to assess the pressure that could be brought to bear on suppliers to meet adequate labelling and packaging requirements.
4. That those present viewed with dismay the fact that representation on the Committee of Transport of Hazardous Materials was confined to government departments only, and that industry as manufacturers, importers, representatives of the FOL and the transport industry be invited to serve on this Committee.

L.H.O.

# Reviews

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## **Emulsion polymerisation: theory and practice**

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**By D. C. Blackley**

**London: Applied Science Publishers Ltd**

**Pp. ix + 566. Price £16.00**

This book is itself a review of published scientific literature with the addition of some of the author's own previously unpublished work. The effect is to give the book a bias towards the emulsion polymerisation of styrene and butadiene for synthetic rubber, but as the author points out, most of the published work relates to this field of application and it also accounts for the largest industrial use of the technique.

The treatment of the subject relates experimental observation to theory where possible—but from the standpoint of batch polymerisation; variations in technique and continuous polymerisation—an important industrial method for preparation of synthetic rubber—are not within the scope of the book.

The first chapter is an introduction, in which terms are defined and the basis for some of the concepts in the mechanism of emulsion polymerisation are presented. This is followed by a short account of the early history of the subject.

The section on the theory of mechanism and kinetics occupies about one-fifth of the text and comprises Chapters 3, 4 and 5 which deal, in turn, with early theory, the Smith-Ewart theory and the Gardon theory. Similarities and differences between the theories are highlighted in the course of the description.

Chapter 6 deals with the process of initiation of free-radical emulsion polymerisation in sections on dissociative initiators—of which the principal example is potassium persulfate—and redox initiators; in a discussion of the latter, an account is given of the mode of action of a varied selection of the many combinations of oxidising and reducing agents, which have been described in the literature.

The effects due to the surfactant component in emulsion polymerisation are presented in Chapter 7. Though both ionogenic and nonionogenic surfactants are covered, there is no discussion, except for a brief mention in Chapter 10, of the use of water-soluble colloids, which are frequently to be found in published formulations of emulsions recommended for use in surface coatings and adhesives.

“Modifiers” having the effect of reducing the molecular weight of the polymer produced, are the topic of Chapter 8. Chapter 9 deals with the effects of electrolytes, alteration of the dispersion medium (by freezing point depressants for low temperature polymerisation), sequestering agents and short stoppers.

“Typical” monomers are treated in Chapter 10, with special reference being made to the effect of water solubility on reaction kinetics, and Chapter 11 reviews emulsion polymerisation in non-aqueous media.

The author concludes with a chapter entitled “Some unsolved problems” and, of the many areas where knowledge of this complex process is still advancing, he discusses mainly reaction kinetics and stereospecific emulsion polymerisation.

The text is well organised and supported by the liberal use of data presented in graphical and tabular form. Each chapter is completed by a list of references. The Contents pages give an excellent guide to the subject matter in each chapter and an index permits location of more specific items. The book is clearly printed and only a few minor misprints were noted.

The book should prove to be a useful basic text on emulsion polymerisation, thus fulfilling the author's hope—expressed in the preface—“that, whether his interest in the subject is mainly theoretical or mainly practical, the serious reader will find in these pages something of interest”.

W. P. J. BAILY

## **Surface characteristics of fibres and textiles Pt. 1**

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**By M. J. Schick (Ed)**

**1975, New York: Marcel Dekker Inc.**

**Pp. xii + 416. Price \$39.50**

It has long been recognised that the surface properties of fibres play a major role in determining the behaviour of the many commercially important fibrous assemblies. Of course, in order to obtain a true picture, surface properties must be considered along with bulk properties, particularly because much of the information on fine structure has been obtained mainly from studies on bulk properties. Because of the vast quantity of literature now available on the science of fibres, however, it is appropriate to devote a monograph entirely to surface properties. Whilst many different techniques have been adopted to study fibre and fabric surfaces, the most important has probably been the development of the scanning electron microscope, and the many SEM photographs included in the present work are evidence of the value of this tool.

The present volume is the work of several collaborators, each one an authority in his own field. The following topics are discussed: friction and lubrication of synthetic fibres, surface properties of cotton and wool, and the surface geometry and scanning electron microscopy of synthetic fibres; the abrasion, resistivity and static behaviour of textile surfaces; applications of the attenuated total reflection technique to the study of fibre surfaces; the effects of photochemical and environmental degradation on the surface properties of fibres; and the colour of fibres and fabrics. A promised second volume will include essays on wetting synthetic fibres; soil release; stain and water repellency; surface properties of glass fibres; the role of friction in the mechanical behaviour of fabrics; and the surface properties in relation to the bonding of “non-wovens”.

As would be expected, there is some overlap in the various contributions, but this is not of importance: each chapter is self-contained and includes a great deal of material, for each subject is treated very thoroughly. The authors have included the most important concepts, but at the same time have given their own particular slant to the subject. This makes the book both authoritative and interesting to read. It is a reliable and comprehensive basic text which will be of value not only as a working document but also as a scholarly reference book. Research and development workers will clearly make most use of such a book, but it will be of assistance to undergraduate and postgraduate students as well as to those in industry, for it sets out clearly the present state of knowledge about an important subject. The editor, a research scientist

with wide industrial experience, is to be congratulated on assembling a collection of extremely well-written contributions, and this volume, together with the promised second one, will constitute a significant addition to the scientific and technological literature.

C. S. WHEWELL

## The measurement of appearance

By R. S. Hunter

London and New York: John Wiley & Sons

Pp. xiv + 348. Price £11.00 or \$22.00

Dr Hunter's prominence in the field of gloss and colour measurement and his contributions to the technical literature over the past 40 years or so must ensure an interested reception for any book published under his name.

"The measurement of appearance" begins by giving a very clearly expressed, but not over-simplified, introduction to the factors affecting the appearance of objects, leading into a comprehensive study of gloss, colour and opacity. Of particular interest to many readers will be chapter 10 headed "Special scales for white colors" and also chapters 8 and 9 on "Uniform color scales" and "Scales for the measurement of color difference", all of which contain details of work carried out during the past 10 years but not hitherto published (to the best of the reviewer's knowledge) in book form.

Inevitably, comparisons will be made with Judd and Wysecki's "Color in business science and industry". Superficially, the two books are similar, inasmuch as they may both be classed as "state of the art" reviews. However, here the similarity ends, the authors' approaches to the subject of appearance measurement being significantly different.

For instance, dealing with gloss, Judd and Wysecki give a detailed account of the application of Fresnel's Law to the assessment of specular reflection, whereas Hunter places more emphasis on the actual measurement of gloss and its relationship to visual appreciation, including useful data not only on colour-measuring instruments but also on light sources, detectors and optical systems.

Similarly, whilst "Color in business, science and industry" devotes a fair amount of space to the derivation of the Kubelka-Munk formula and its application to colour and opacity, "The measurement of appearance" lays more stress on instrumental methods of measurement and their correlation to subjective appearance.

This difference in approach not only makes the two books in a sense complementary (what cannot be found in one will almost certainly be in the other), but may also be expected to ensure "The measurement of appearance" a position in its own right on the bookshelves of those connected with the technical side of the surface coatings industries.

A. J. FORD

## Information Received

### Cis-Tek agency for Swedish firm

Cis-Tek Ltd, Dunstable, Bedfordshire has been appointed the exclusive UK agency for the Swedish firm AB Casco's complete range of "Svedorit" synthetic resin films. These melamine-based films are used extensively in the manufacture of low and high pressure laminates and in the production of melamine-faced chipboard. Other types of resin films available include synthetic veneers, chipboard surfacing films (for subsequent over-lacquering) and overlays.

### Guest Industrials—change of address

Guest Industrials Ltd, Raw Materials Division, has now reoccupied its old offices and the company's address reverts to: Tubbs Hill House, London Road, Sevenoaks, Kent TN13 1DE.

### Hygrotherm orders from South America

Two new orders from Ecuador bring up to £250 000 the total value of South American contracts in the past 12 months for Hygrotherm Engineering Ltd synthetic resin production plant. Previous orders were from Venezuela and Peru. During the 25 years that Hygrotherm has been designing and supplying plant for the manufacture of synthetic resins, used principally in the paint industry, the company has been responsible for installations in almost every part of the world.

The two new orders are both from Guayaquil, Ecuador. They are for plant for a new resins factory and for a small universal research unit for the Faculty of Chemistry at the University of Guayaquil.

### Jacobson—change of address

Following the parent company's merger in Holland, the Chemical Sales Division of

Jacobson van den Berg & Co. (UK) Ltd has moved to the spacious new premises of its sister company, R. S. Stockvis & Sons Ltd. The sale of chemicals will be handled by:

Jacobson Chemical  
R. S. Stockvis & Sons Ltd,  
Pool Road, East Molesey, Surrey KT8  
0HN (Telephone: 01-941 1212. Telex:  
917116).

Extensive chemical stocks will also be located at this address. The accounts section will remain at Jacoberg House in London.

### New jaw crushers from Glen Creston



An example is shown above of the latest series of Glen Creston jaw crushers, which combine compactness with sufficient strength to crush fist-size rocks to fragments less than 1mm in size in one pass.

### New factory for Kenroy Dispersions

Kenroy Dispersions Ltd has announced that, due to continued expansion, it has acquired a new factory to increase production capacity. Correspondence to Kenroy Dispersions Ltd should now be addressed to: Holt Mill Road, Waterfoot, Rossendale, Lancs BB4 7JB.

### New pilot plant for CIBA-GEIGY Pigments Division

A new pilot plant has been commissioned at the manufacturing site of CIBA-GEIGY's Pigments Division at Hawkhead Road, Paisley. The pilot plant, which has cost over £800 000 to build, provides facilities for the development of new products, improved processes and techniques.

The growth and increasing complexity of pigment manufacture has called for specialisation in process development and the new pilot plant marks a major stage in the establishment of process development within CIBA-GEIGY. The new plant will enable the development of processes which are safe, reduce manufacturing costs, can be effectively controlled, allow an improved working environment and eliminate or control undesirable effluents.

### Propylene oxide manufacture

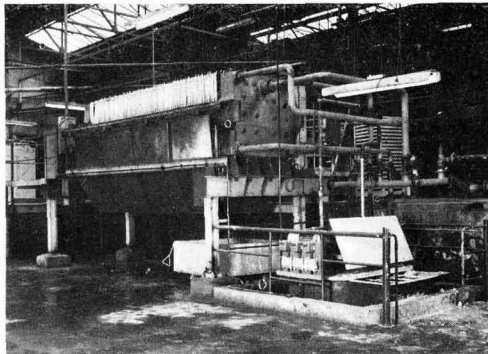
Solvay & Cie, Laporte Industries (Holdings) Ltd and Carbochimique are collaborating in research work to develop a pilot plant for the manufacture of propylene oxide.

### Victor Wolf Ltd appointed agent for Meister

Victor Wolf Ltd, Clayton, Manchester, has been appointed the sole UK agent and distributor for the Meister AG (Basle) range of organotin biocides and fungicides.



The new pilot plant at the site of CIBA-GEIGY's Pigments Division, Paisley (see page 180 opposite)



The new, large capacity, automated filterpress installed at the Stockport factory of Burrell & Co. Ltd as part of a recently completed £500 000 investment programme to improve methods of production with an emphasis on health, safety and environmental aspects, higher output capacity and swifter delivery to customers

The full range of 10 products is available, for use in latex, marine and antifouling paints. The products are also widely used in the fungicidal and insecticidal treatment of wood, paper and textiles.

The BS101 grade is particularly recommended as an additive for PVC plastisol coatings and PVC film paints. The facilities of both Victor Wolf Ltd and the Meister AG laboratories in Switzerland will provide a full technical service to users.

#### Death of Dr Cornelius

With regret, the recent death is announced of Dr E. G. Cornelius, chairman and founder of the Cornelius group of companies.

### New products

#### Low toxicity solvents

Carless Solvents Ltd, of Harwich, a wholly owned subsidiary of Carless Capel & Leonard Ltd and one of Britain's leading producers of hydrocarbon solvents, has introduced a new range of low toxicity solvents under the name "Clairsols".

Clairsols are produced from carefully selected feedstocks, which undergo special processes resulting in fractions of high purity and very low aromatic, olefin and sulfur content.

#### New ink from Fishburn

Fishburn Printing Ink Co. Ltd has introduced under the name "Black Prince" a new, versatile, non-heatset, web-offset black ink to supersede the company's "Newsking" blacks.

#### Two new pigments from CIBA-GEIGY

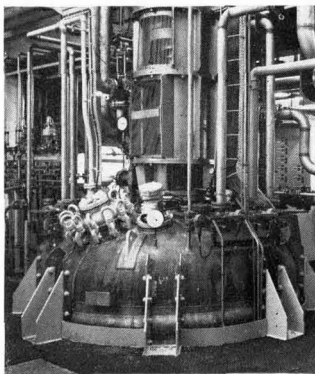
Two new additions have been made by the Pigments Division of CIBA-GEIGY to its range of pigments for paints.

Irgalite Yellow PDS8, an arylamide G pigment, is an addition to the Irgalite PDS range of easily dispersible pigments for paints. It is a high strength product with a reddish hue.

The other new addition, Irgalite Yellow GO was developed especially for the production of strong yellow shades in decorative paints, where good opacity and low toxicity are the basic requirements. It is a strong, bright, mid-shade arylamide yellow pigment.

#### Major increase in emulsion capacity for Vinyl Products

Vinyl Products Ltd has recently commissioned a £1 million extension to its factory in Eastford Road, Warrington, Cheshire. The new plant gives the company an additional 10 000–11 000 tonnes annual production capacity for water-based polymer emulsions. Its location in north-west England, with the company's main plant in the south-east, greatly helps in strengthening delivery service. The extension consists basically of new reactor facilities, housed in a building with 650m<sup>2</sup> floor space, and a bulk storage unit with a holding capacity of approximately 400 tonnes.



Part of the new Vinyl Products Ltd production unit

### Conferences, courses, etc.

#### Colour and materials conference in Germany

The Deutschen Farbzentrum (German Centre for Colour) will hold a Conference, with the theme "Colour and materials—technology and production", at the Bundesanstalt für Materialprüfung in West Berlin from 1 to 3 November 1976. Within the theme of the Conference, the meeting will be organised into sessions on architecture, illumination, coatings technology, chemistry of dyes and pigments, design of capital and consumer goods, colour measurement, art (both papers and display), and techniques of reproduction by printing, photography and television.

#### Colour education

A symposium of the Colour Group to be held on 1 and 2 October 1976 at the Normandy Hotel, Renfrew, will include papers on aspects of the use of colour in education and the basic principles of colour science, language and technology.

#### USA coatings symposium

Mr Z. W. Wicks Jnr has kindly informed us that the 16th annual Coatings Symposium of the North Dakota State University will be held in Fargo, North Dakota, USA, from 2 to 4 June 1976, under the title "Energy savings through reactive coatings". Anyone wishing to attend should as soon as possible contact the Director & Secretary at the address on the Contents page of this issue.

### Literature

#### BSI publications

The following are now available:

*BS 3981: 1976 Iron oxide pigments for paints.* This standard has recently been revised and now adopts fully the international standard ISO1248. The price is £2.40 including postage.

*BS 3900 Methods of test paints, Part A8. Determination of the danger classification by flashpoint (closed cup method)* has also been

revised. This part now constitutes the English text of the European standard EN53 and is identical with the 1968 edition so far as the procedure is concerned. It is, however, no longer restricted to the Abel closed cup, the new edition allowing the use of other standard closed cups which are known to be satisfactory. Price £1.50.

*BS 4800 Paint colours for building purposes. Supplement No. 1. Table of colorimetric values of colours to BS 4800.* This recently released supplement gives chromaticity co-ordinates and luminance factor values expressed in terms of the trichromatic system for colorimetry established in 1931 by the International Commission on Illumination (CIE) using standard illuminant D65. Price £0.75.

#### Bladder tumours

The Chemical Industries Association has published an updated guide dealing with the cause and prevention of bladder tumours in workers in the dyestuffs and related industries.

#### Consulting scientists and contract research organisations

Fulmer Research Institute Ltd has published the third edition of its register of consulting scientists and contract research organisations. In the new edition, there are some 50 new subjects on which expertise is offered and approximately 100 new names. The editorial section includes the recommended code of practice for consultants and others offering scientific and technical services. The price is £7.50 including postage and packing.

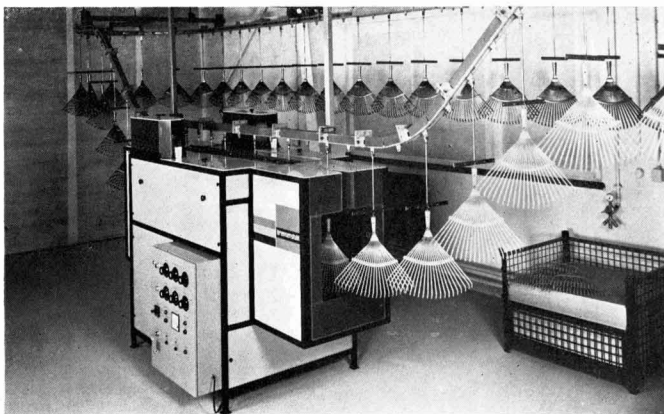
#### Profile of the UK paint industry

Information Research Ltd has published the fourth edition of its marketing research report on the UK paint industry. In a summary, it indicates that the demand for all types of paint in the UK is expected to grow from the 1975 level of almost 700 million litres to around 885 million litres by 1980 and 1075 litres by 1985. The extent of the scope for greater usage is said to be confirmed by the fact that the annual *per capita* consumption of paint (just over 13 litres) is still well below that of many other European countries. The average annual growth rate of the various main types of paint over the next few years is expected to be as high as seven per cent for decorative emulsion paints, but barely more than two per cent for gloss paints and some specialist materials, although the industrial sector will grow at six per cent per annum. Decorative paints will continue to be the major usage sector and will account for almost 550 million litres of the market in 1980, with water-based emulsions slightly exceeding the level of traditional gloss paints. On the industrial side, it is expected that powder coating processes and electropainting methods will assume much greater importance into the 1980s.

Copies of the report are available at £22.50 each.

#### UK chemicals 1975-1985

The National Economic Developments Office has issued a 100-page report "UK Chemicals 1975-85: strategies and opportunities for the industry", prepared by a working party under the chairmanship of Mr S. Woodhams, senior vice-chairman of Fisons Ltd. Copies are available at £2.74 (postage paid) from Neddy Books, NEDO, Millbank Tower, London SW1P 4QX.



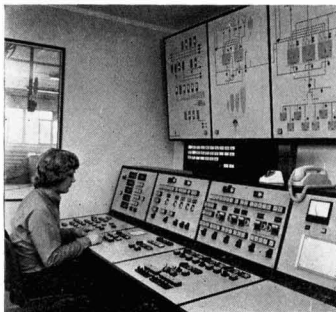
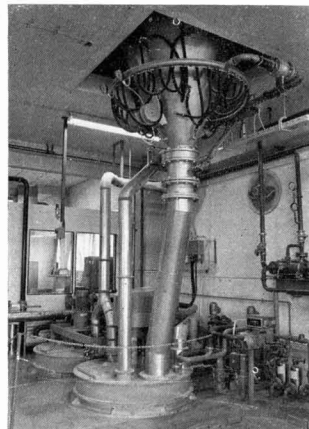
The new "BPE 810" electrostatic powder coating system recently introduced by Lectra Technik AG of Switzerland

The movable unit can be set up in any sufficiently large room and needs only the provision of an electric socket. The charge of powder coating is raised electrostatically in a closed spray cabinet for pre-set time and the work-piece, which hangs in the cabinet, receives an equal thickness of coating from 50 to 300µm. Colour changes can be performed in a few seconds simply by replacing the spray cabinet. The BPE 820 is an automatic version of the machine.

#### Norwegian firms exhibit advanced process control equipment at OCCA-28

A computer-controlled fully automated production line for paint has now been put into commission at A/S Jotungruppen's factory in Sandefjord, Norway. The process control and manufacturing technology on which this new plant is based was developed by the two Norwegian firms Noratom-Norcontrol A/S and A/S Jotungruppen jointly. The computer-controlled production line, which is believed to be one of the most sophisticated in the modern international paint industry, makes bases which provide the foundation for further manufacture. With the new system only nine formulations, giving nine different bases, will be required. Through intermixing processes, these will yield the same number of varieties of product (so far as colour, gloss, etc are concerned) as the 100 formulations did previously.

See also the Exhibition Report under "Manufacturing equipment" on page 188.



From the control room (left), the operator can supervise the simultaneous production of up to three bases and look through a window to (top) where the correct quantities of resin, solvent, etc are automatically metered into the mixing and dispersion vessels. The bottom right-hand photograph shows the tanks for storing the final bases

# STOP



The decisions you make today will affect the success you can achieve tomorrow. And the future lies with environment-friendly cost saving paints. So stop! Make the right choice.

Our High Solid Resimene Resins present you with all you need: no environmental problems, a full range of reactivity and a new level of crosslinking efficiency. You can even benefit by introducing them in the conventional paints you are using now and they could be your starting point for medium solid paints.

So send for more technical information, or ask for a test sample now!

From the 25 High Solid Resimene product line, could you provide me with a sample of your best proposal for a fast curing RESIMENE  for a medium curing RESIMENE  for a slow curing RESIMENE  to solve the following problem:

Name \_\_\_\_\_

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**Monsanto Europe S.A. Resins & Specialties**  
 Department Avenue de Tervuren 270-272, LB 1  
 B-1150 Brussels (Belgium)

J1234

# Monsanto



# CLAIRSOLS<sup>®</sup>

**THE CLEAN AIR  
SOLVENTS**

Carless have developed a range of solvents that meet 'Clean Environment' requirements. Clairsol close cut fractions offer good solvency, odour, colour, with very low aromatic and olefin content ensuring minimal toxicity and pollution.

For further details please telex, phone, or write to Chris Smith or Ken Wiseman, Carless Solvents Limited, Petrol House, Hepscott Road, Hackney Wick, London E9 5HD. Telephone: 01-985 5500. Telex: 261071.

*Another first from Carless*

**CARLESS**





The Exhibition Committee is pleased to report that, despite the economic recession, exhibits from the UK and 15 overseas countries were on display at the OCCA-28 Exhibition of raw materials and equipment for the surface coating industries, which took place at Alexandra Palace, London from 23 to 26 March 1976.

## 'MANY NEW EXHIBITORS'

A pleasing feature was the large number of new exhibitors and past exhibitors who did not participate in OCCA-XXVII, so that visitors found a great deal of new and interesting material on display. The Committee emphasises that the Rules governing this unique annual function stipulate that, as well as new products, new information on existing products and information not readily available are equally acceptable, and it believes that discussion about products with technical personnel on the Stands is of vital importance. For many years, the Exhibition has been known as the international forum for technical display and discussion in the surface coating industries, and the Committee is convinced of the necessity for providing an annual focal point at which the continuous dialogue between the raw material suppliers and

## 'INVALUABLE IN TERMS OF COST-EFFECTIVENESS'

manufacturers of surface coatings can take place. One exhibitor commented that the value to him of bringing together so many technical personnel at this event was incalculable when he considered the cost involved in sending representatives to the countries from which visitors were drawn.

Among the overseas visitors, representatives from the following countries either signed admission tickets or the Visitors' Book at the Association's Information Centre:

# OCCA-28

Alexandra Palace, London. 23-26 March 1976

## Exhibition Review

★ Australia ★ Austria ★ Belgium ★ Denmark ★  
★ Germany ★ Greece ★ Hungary ★ Italy ★  
★ Norway ★ Poland ★ Romania ★ Spain ★  
★ Sweden ★ Switzerland ★ UK ★ USA ★

Australia, Austria, Belgium, Canada, Czechoslovakia, Denmark, France, Finland, Germany, Greece, Holland, Hong Kong, Hungary, Iceland, Iran, Iraq, Ireland, Israel, Italy, Jamaica, Japan, Jordan, Libya, Morocco, Norway, Poland, Portugal, Romania, South Africa, Spain, Sweden, Switzerland, Turkey, USA, Venezuela, Yugoslavia, Zaire.

Both exhibitors and visitors have expressed their pleasure at the facilities offered by Alexandra Palace where the Association's Exhibition was the only one being held during the week, so that full advantage could be taken of all the facilities, which included two restaurants, two bars, a cafeteria, unlimited free car parking, and the Association's free bus service to and from Turnpike Lane Station on the Piccadilly line underground. As the weather was fine for most of the days, many visitors were able to enjoy a walk along the South Terrace and were able to view the Palace

grounds where spring flowers were in evidence on the slopes.

Preliminary arrangements have been made for OCCA-29, which will take place at Alexandra Palace, London from 22 to

## 'WE'LL BE BACK IN 1977'

25 March 1977, and the Association has already received a number of enquiries both from exhibitors at OCCA-28, who wish to be allocated Stands again in 1977, and from other organisations wishing to show.

In pursuance of the above theme, the special motif of the 1977 Exhibition will draw attention to the way in which visitors

*(Continued on page 191)*



A view of the main hall at Alexandra Palace showing the Association's Information Centre, one of the crowded corridors, and one of the two seating areas provided for visitors to meet friends and consult literature between visits to Stands

## Exhibition Report 1976

**Additives, driers, surfactants and hardening agents** ★ **Chemical intermediates** ★ **Extenders, fillers and matting agents** ★ **Laboratory apparatus and testing equipment** ★ **Manufacturing equipment, drums, etc.** ★ **Pigments** ★ **Resins—acrylic, alkyd, amino, emulsion and water based, epoxy, miscellaneous, polyamide** ★ **Solvents and plasticisers** ★ **Technical journals and services**

### Additives, driers, surfactants and hardening agents

CHEMETRON CORPORATION has introduced polyethylene compounds for solvent and water-based systems, which provide slip and pigment suspension properties.

CHEMOLIMPEX exhibited single and mixed metal versates for use as driers, and a range of catalysts including methyl ethyl ketone, cyclohexanone, benzoyl and mixed MEK-CH peroxides.

COLE CHEMICALS LTD, formerly the trading division of R. H. Cole Ltd, showed a range of additives, manufactured by PLAST-LABOR of Switzerland, and speciality additives and preservatives from the TROY CHEMICAL CORPORATION of the USA.

DOW CHEMICAL EUROPE showed the "Dovicile" 75 in-can preservative and S 13 fungicide, the Methocel J series of cellulose thickeners for latex paints, and an experimental synthetic thickener for the same purpose, which gives better rheological properties for one-coat application. The experimental hardener XD 8062.00 has been developed for cross-linking epoxy powder coatings, and the curing agent XD 7080 for use with acrylics and epoxies in water-based coatings is another experimental product.

DURHAM RAW MATERIALS LTD featured a display of materials useful in the field of biodeterioration of paints and allied products, with particular reference to the non-toxic replacement of mercurials, and introduced a new non-toxic agent, "Nuosept 95". Information was available on the "Nuodex" and "Curwen" ranges of driers, the "Nuodex" range of additives for various purposes and the DURHAM range of metallic soaps.

HERCULES POWDER COMPANY LTD gave information on its thickener/stabiliser systems in emulsion formulations and its new range of "Picconol" resin dispersions.

JACOBSON VAN DEN BERG & CO (UK)LTD exhibited the "Surfynol" range of non-ionic surfactants based on tertiary acetylenic glycols from the Acetylene Chemicals Division, the "Dabco" catalysts and the LK series of non-silicone surfactants for polyurethane foams from the Chemical Additives Division. The INTERNATIONAL GENERAL ELECTRIC CO's range of silicone fluids and emulsions to improve flow, gloss, pigment dispersion, anti-foam and bubble control additives and silicone water repellents were shown. Information was available on the LOMBARD-GERIN corrosion inhibitors to prevent can corrosion and the flash rusting of steel substrates, the POLYCHIMIE range of polyethylene wax dispersions to improve rub and scratch resistance and high melting wax dispersions for wallpaper coatings, as well as the SUPERCOLORI SPA series of anti-settling and thixotropic agents for solvent based products, defoamers, pigment dispersants, and the SUDPLAST plasticiser for water-based coatings.

JB LABORATORIES (incl. MICRON SERVICES) has available organophilic and water soluble, clay-based gellants, which are supplied in the dry or paste form.

MONSANTO EUROPE SA demonstrated the "Modaflow" and "Multiflow" series of flow agents for non-aqueous industrial coatings, used in concentrations of 0.1 to 2 per cent based on the resin solids content, to give smooth films and which are easily incorporated into many thermosetting and thermoplastic resins. Modaflow powder is an additive to reduce surface imperfections in industrial powder coatings and has all the advantages of Modaflow liquid, but is more easily incorporated because of its powder form.

TITANIUM INTERMEDIATES LTD displayed a wide range of titanium chemicals mainly associated with catalysis and crosslinking, to produce faster curing, reduced water sensitivity, improved impact resistance, film stability, adhesion, flexibility and lower curing temperatures.

UCB SA exhibited the "Uvecryl" series of photoinitiators and photoactivators, and has available acrylated oligomers and acrylated polyfunctional monomers.

### Chemical intermediates

ARCODE LTD exhibited a number of pigment intermediates, maleic and phthalic anhydrides and other chemicals for the paint, varnish, plastics, rubber, printing ink and insecticide industries.

COLE CHEMICALS LTD is able to supply vinyl acetate monomer manufactured by SISAS of Italy and the WESTVACO lignin-based chemicals.

LAPORTE INDUSTRIES LTD showed caprolactone and a range of polycaprolactones manufactured by INTEROX CHEMICALS LTD at Warrington. These products are intended for polyurethane systems and for the modification of a wide range of surface coating resins. Caprolactone reacts readily with hydroxyl and amino groups to give polyester chains terminated by primary hydroxyl groups; it can be used to modify a wide range of resins, where improvements in flexibility and impact strength are sought. Since it is also an excellent high boiling solvent of low odour and toxicity, it is under investigation for other applications, such as vinyl lacquers, etc.

MONTEDISON GROUP gave information on a range of intermediates and chemicals for industrial purposes, including pentaerythritol, trimethylol propane and maleic anhydride.

TITANIUM INTERMEDIATES LTD showed a wide range of titanium-containing chemicals (see under "Additives").

UCB SA has a range of monomers, including acrylated polyfunctional monomers, polyol acrylates, polyester acrylates, polyurethane acrylates, epoxy acrylates, and acrylated oligomers.

WARWICK CHEMICAL CO. exhibited its range of chemical intermediates for manufacture under contract.

### Extenders, fillers and matting agents

HOPTON MINING COMPANY LTD demonstrated the results of 50 years' trading in the field of powder technology, with particular reference to the process of micronisation to produce easily dispersible products. The company will continue its policy of providing competitively priced extenders and fillers of high quality and of offering advice on the solution of the problems of individual users and industries.

JACOBSON VAN DEN BERG & CO (UK) LTD exhibited the ARMOFORM light-weight glass microballoons for use as fillers, and the CARGAS INORGANICAS SA range of micronised barytes and gypsum for use as extenders.

### Laboratory apparatus and testing equipment

WILLY A. BACHOFEN exhibited a laboratory model KDL of its Dyno-Mill having a capacity of 0.6 litres with an output of 21 litres per hour with the minimum batch size and 15 litres per hour at the maximum size (see "Manufacturing equipment").

CONTRAVES INDUSTRIAL PRODUCTS LTD showed a range of laboratory viscometers, including the "Rheomat 30" 30-speed instrument, covering a wide range of shear rates and shear stresses with a selection of interchangeable measuring systems; it may be used with a versatile programmer and an X-Y recorder for the automatic plotting of rheograms. The "Rheomat 15" with a synchronised chart recorder is a 15-speed instrument for a wide range of general purposes and research. The TV and STV are single- and three-speed instruments for relative, and absolute viscosity determination for quality control purposes. The Balance Rheometer is an oscillation rheometer for determination of the viscoelastic properties of resins, high polymers, gravure inks, etc.

D. H. INDUSTRIES LTD included in its exhibit the small PAUL VOLLRATH mixers, with a 0.23 W motor (see "Manufacturing equipment").

DIFFUSION SYSTEMS LTD exhibited surface measuring equipment applicable to the paint, plastics, paper and printing industries, which include spectrophotometers, reflectometers, densitometers, gloss meters, haze meters and photometers. New additions are the DS 29 Universal digital read-out, as an alternative to the Unigalvo 20 or 200, and 75° and 85° glossheads to TAPPI and ASTM specifications.

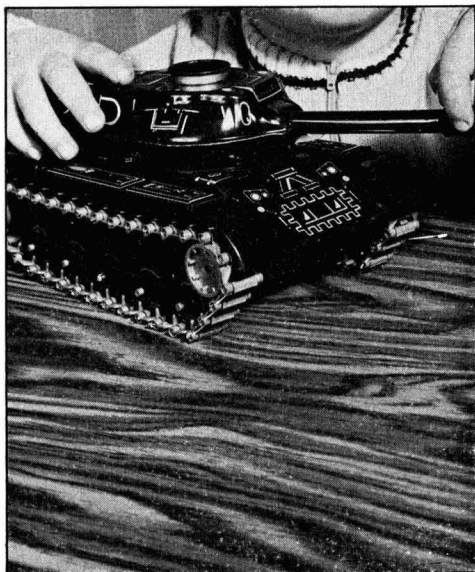
ELCOMETER INSTRUMENTS LTD showed its new Minitecor 151 series for measuring the thickness of coatings applied to all types of metallic substrates. Also exhibited were the Roughtector for measuring surface roughness on all types of surface, but especially on steelwork after blast cleaning. Instruments for measuring wet film thickness, surface cleanliness, pinholing and porosity detection were displayed, as well as the TABER abramer and ERICHSEN testing equipment. Also shown

# Matt matters

*\*GASIL controls surface shine in many applications:*

## Wood lacquers

Furniture manufacturers require matt lacquers which will stand rough treatment without scratching or lifting from the substrate. Gasil users don't have these problems — and the high quality of their lacquers is reflected in the clarity of the film.

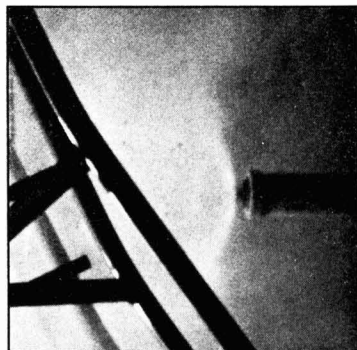


## Washable wallpaper

Gasil WP can be stirred in to emulsion based top coatings to give matt wallpapers of brilliant clarity and natural appearance, with improved resistance to water and grease stains.

## Plastisols for metal

Hard working metal surfaces need the protection of a durable thick coating and plastisols are often chosen for this purpose. Such coatings are effectively matted with larger sized Gasil products without adversely affecting the rheology of the system.



## Powder coatings

Conventional matting agents are unsuitable for most powder coatings and Crosfield has developed silicas which offer a high degree of gloss control. Crosfield's long experience in solving industrial caking problems enables us to give practical advice on ensuring good powder flow.

*\*Gasil is a proprietary brand name.*

*Talk to Crosfield about your surface problems. With the Gasil range of Micronised Silica Gels we can give you the benefits of years of research.*



# White on cue...

You'll win every time with EWO® barytes, the ultra-white extender/filler from Sachtleben. EWO® is a natural, highly dispersed barium sulphate powder obtained from our own white spar deposits and specially processed to BS 1795-1965 for exceptional fineness.

Its properties make it particularly suitable for use in vinyl silk finish emulsion paints as well as in other types of paints, dry colours, adhesives, papers and rubbers and plastics.

Additional useful characteristics include a consistent particle size (max. 20 µm); low absorption of binders; minimal agglomeration and easy wetting and dispersion. Sachtleben won't snooker you for supplies for, like all our products, EWO® is always available right on cue.

You'll probably be in pocket, too, for EWO® bulk prices are really competitive. Why not make contact with Brian Mayhew today at the address below? He'll send you full information and frame a quotation for you. If EWO® isn't the filler/extender you need, ask him about barium sulphate in Albaryt, Fleur and Barytmehl grades.



» **SACHTLEBEN** «

Sachtleben Chemie GmbH,  
U.K. Sales Office, 56 High Street,  
Edenbridge, Kent TN8 5AJ.  
Telephone: 073-271 3694 Telex: 95297.

Manufacturers of Hombitan TiO<sub>2</sub>, Sachtolith, Lithopone, Blanc Fixe, Albaryt & EWO grades of White Barytes.

were Q-panels Q-U-V accelerated weathering tester, which alternates UV irradiation from a special fluorescent tube with condensation cycles, and the steel and aluminium test panels. The NEOTEC Duicolor colour difference meter was also shown.

JOHN GODRICH demonstrated a working model of the Rotostat 05 laboratory mixer (see "Manufacturing equipment"), and were able to provide information on the Suntest and Xenotest light- and weatherfastness testers, salt spray and SO<sub>2</sub> cabinets and other types of laboratory equipment.

JB LABORATORIES, including MICRON SERVICES, is able to provide: micronizers, in conjunction with AIR-FILCO, which can operate in air, steam or nitrogen atmospheres to cater for heat sensitive materials; a homogeniser from ALM Paris for all pigment and paint dispersions; colloid mills by PROBST & CLASS for high speed dispersion in the paint and allied industries. All these have been scaled up for factory operation. Also available is the SHARPLES laboratory super centrifuge.

MANUFACTURERS ENGINEERING AND EQUIPMENT CORPORATION displayed the Model V Colourmaster for fast and accurate colour measurement, with reflectance or transmission readings, and stressed simplicity in operation with high precision at all colour levels and uniformity of performance.

MILLROOM ACCESSORIES AND CHEMICALS LTD included in its exhibit a range of laboratory equipment, which included the Rotamix SM 4 and the Whirl, pot mills and pot mill rollers (see under "Manufacturing equipment").

RESEARCH EQUIPMENT (LONDON) LTD exhibited the latest examples of its laboratory instruments, which include the cone and plate viscometer, drying time apparatus, micro-indentor and pressure wt/gal cup, all developed by ICI LTD, and a selection of REL apparatus, including scratch and impact testers, abrasion testing apparatus, flow cups, fineness of grind gauges and single- and double-head metering pumps.

SCIENTIFIC AND EDUCATIONAL AIDS (ABR) LTD showed for the first time at the Exhibition and exhibited a range of laboratory apparatus, including the SEA laboratory furnaces, dissolved oxygen meters, laboratory and industrial balances, from analytical models to 11kg top pan units.

WENTWORTH INSTRUMENTS LTD exhibited for the first time in Europe the new GARDNER XL-20 tristimulus colourimeter which features a new optical system incorporating thermally controlled filter/detector combinations to minimise drift and improve stability. It can be interfaced with the HEWLETT PACKARD 9810 Programmable Calculator to form the XL-30 colourmeter/computing system. Also shown was the GARDNER multi-angle digital glossmeter, together with the Glossgard photometric system, and the new bench-top model (4682) of the RESEARCH INC. high intensity infrared researched system—a new modular system, which is a major advance on existing electrically or gas-heated hot air ovens. Multiple heat zones are available, using the Pyropanel self-

cleaning ceramic reflectors with tungsten-quartz heating elements above and below the conveyor belt. Also shown was the ATLAS Compact Weather-Ometer and the Kesternich (50) SO<sub>2</sub> corrosion test cabinet to DIN 50 017/018, which is to become an ISO standard test, and is being written into BS 3900. A modification to this instrument is available, to adapt it for service as a salt fog tester to ASTM B117 and B368, DEF 1053 Methods 24 and 26, DIN 50907 and 50021, and a number of other recognised standards.

UCB SA demonstrated typical UV systems using the WALLACE KNIGHT Labcure system.

### Manufacturing equipment, drums, etc.

WILLY A. BACHOFEN exhibited the "Dy-no-mill" horizontal bead mills of compact size, which need no foundations and are portable. A mill of 15-litre capacity is claimed to have an output equivalent to a 50-litre sand mill. The machine can operate continuously or process numerous small batches in quick succession. Cleaning is rapid and uses little solvent. Four sizes of mill were exhibited, having capacities of 0.6, 5, 15 and 45 litres. A new cooling cylinder has been introduced for the milling of temperature-sensitive products.

WILLIAM BOULTON LTD showed its range of vibratory equipment, which includes a vibratory machine for colour coating of polymer granules or powders, a vibratory grinding machine for coarse or fine grinding, the PODMORE/BOULTON "Vibro-Energy" mill for grinding to submicron sizes, a Vibro-Energy strainer for solid/liquid separation, a separator for solid/liquid separation and solids classification, and an oil/water separation system, which can reduce oil pollution to as low as 2 ppm. Information was available on a wide range of other equipment.

COLE CHEMICALS LTD displayed the ROSENTHAL STEMAG grinding media from West Germany.

CONTRAVES INDUSTRIAL PRODUCTS LTD displayed its "Covistat" industrial viscosity regulator for use in open tank applications, with a remote recorder and control unit and the DC series of process control viscometers for continuous in-line viscosity measurement (see also under "Laboratory apparatus").

D. H. INDUSTRIES LTD gave details of a wide range of equipment, which included: the SUSSMEYER sand and micro-element mills, now available with hydraulic drive and with new washing equipment; solvent recovery plants with up to 900 litres per hour output; resin plants with either gas, oil or induction heating; the "Centrimill" batch bead mills; high speed cavitation mixer/dispersers and low speed, high torque mixers with "bowtie" blades; the J. DE VREE weight and volumetric filling machine with automatic tin feeding, adhesive-tab colour or batch marking, automatic lid dispensing, batch number marking, and with facilities for packing and sealing filled tins into cartons; the PAUL VOLLRATH two-speed and variable speed mixers, from 0.2 to 150 kW, and the EXENTRIC dual-shaft dissolvers. Also available were the CUNO filters, PREBA filter, the KUPPER heavy duty Z-blade

mixers, the PAMASOL WILLI MADER aerosol filling plant, from the laboratory scale model upwards, and the DUNO range of shredding machines, together with compactors for tins, plastics, bricks, wood, tyres, etc.

DIAGA/S exhibited the MAXFILL weight filling machine, covering a range from 2.5 to 50 kg at a rate of approximately 180 litres per minute, which can be supplied with a special device for foaming products, and a lid closing machine for flanged or other types of lids. Information was available on stationary and portable mixers, from 0.75 to 200 kW, bead mixing mills and vibratory sieves (see also under HERBERT SMITH & CO.).

G. J. ERLICH LTD gave information on the full range of MOLteni plant, with special attention given to the new planetary mixers of capacity above 500 litres, where a fully enclosed hydraulic drive replaces the mechanical, variable speed drive; the oil tank and power pack are at the rear of the machine to facilitate operations and there are no trailing hydraulic pipes. Information was available on a series of filling plants, screens, grinders and vessel cleaning plant. The MOLteni high-speed disperser of 600 litres capacity was shown. This can operate under vacuum at speeds ranging from 400 to 2000 rpm. A fully automatic machine for filling pastes into cartridges, cans or drums was also on view.

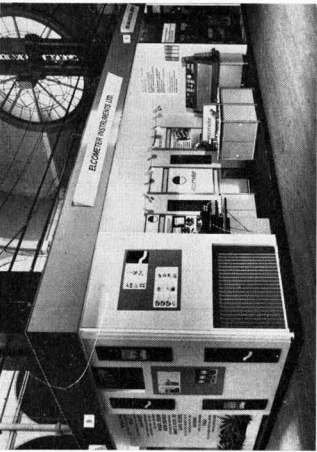
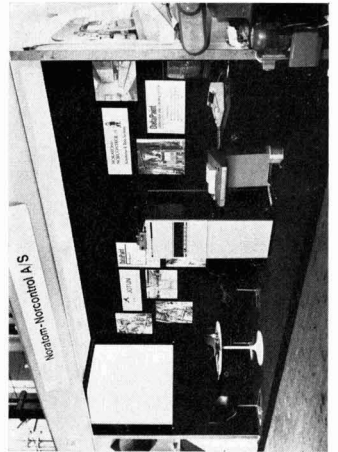
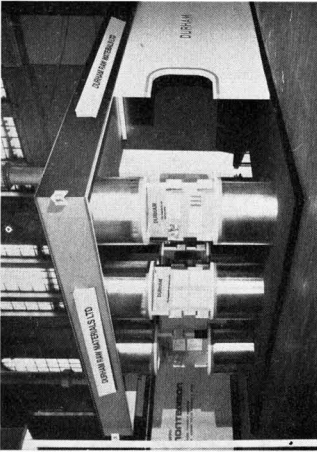
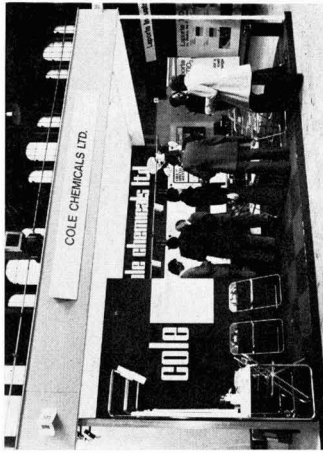
JOHN GODRICH showed the CHEM-COL mixers, in which there are no bearings in the immersed part and in which the flow pattern can be from top and bottom or from the top or the bottom only, to eliminate aeration. Several designs of rotor are available for use in accordance with the type of liquid involved. The new "Rotostat" mixing machines are designed to process materials of high viscosity and to facilitate cleaning; they have no suspender-basket assembly and this allows better flow characteristics. A laboratory model 05 was demonstrated in operation, and larger models 10 and 30 are available.

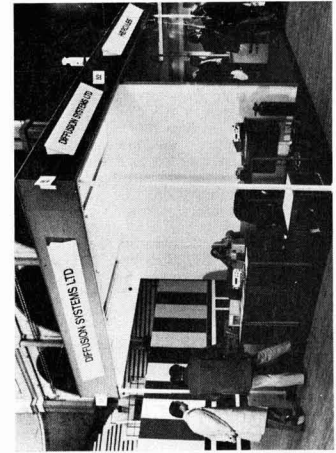
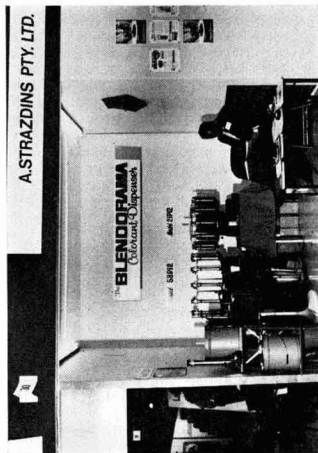
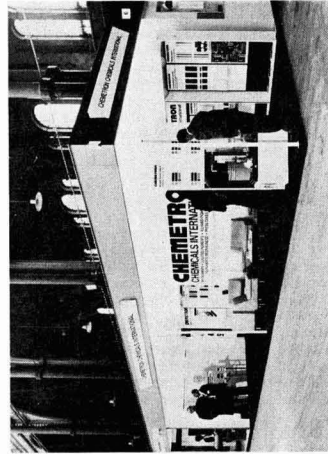
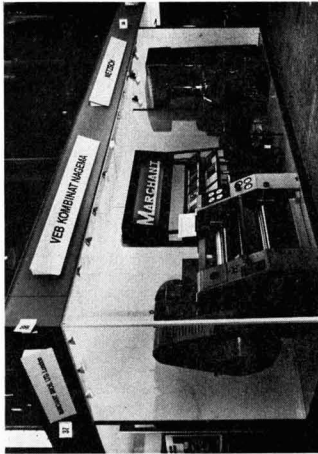
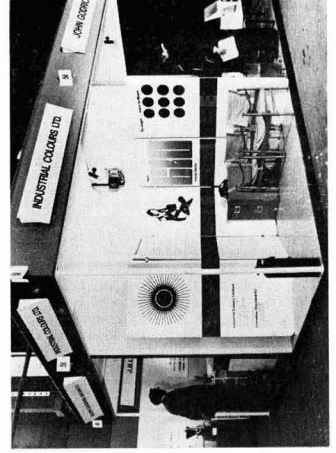
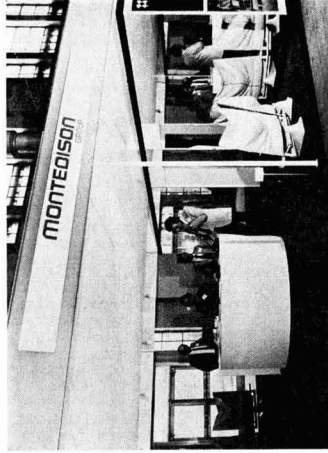
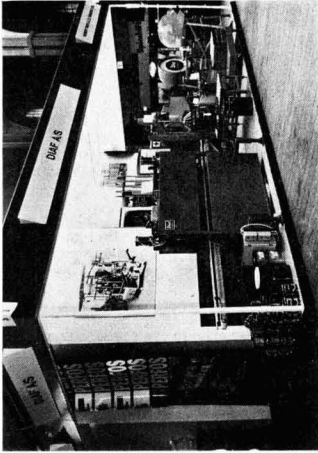
The JB LABORATORIES (MICRON SERVICES) apparatus described under "Laboratory apparatus" has been scaled up to give outputs in the range of several tonnes per hour.

VEB KOMBINAT NAGEMA exhibited machinery manufactured by MASCHIN-ENFABRIK HEIDENAU. Triple rolls available in the inclined "L" form are made in roll sizes: 320 × 800mm (NVH 813/1) and 400 × 1000mm (NVH 913). The L-shaped roll facilitates product handling and economises in floor space. The mills are fitted with chill-cast rolls, two-speed drive via a clutch and gearbox, and hydraulic roll pressure control. A new mill being developed in the horizontal range is likely to have a roll size of 300 × 610mm. This equipment is distributed in the UK, Canada, Eire, Portugal, Spain and the USA by MARCHANT BROS LTD.

JACOBSON VAN DEN BERG & CO. (UK) LTD provided information on the RUDOLF NEULINGER bead mills, high shear impeller mixers, planetary kneader mixers and triple roll mills.

MARCHANT BROTHERS LTD gave information on the plant and machinery available to the printing ink, paint, plastics, ceramic, cosmetic, confectionery and paper industries. The MARCHANT Service and





Spares Department provides, in addition to machinery maintenance, the overhaul of roll mills, camber roll grinding, the overhaul of mixers and a comprehensive factory installation and removal service. The NETZCH/JOHN system, agitator mill was also exhibited. It is intended for use with highly pigmented, temperature sensitive paints and printing inks. The main advantage is annular dispensing chamber with central water cooling.

A new horizontal closed continuous mill has been added to the range of "Master-mills" manufactured by the MASTERMIX ENGINEERING CO. LTD. It has many novel features and can achieve an output of two to three times that of conventional sand mills; it can handle viscous or thixotropic material, and solvent losses can be almost totally eliminated; and it includes special cooling. Many types of internal construction are available, including stainless steel, manganese steel, ceramic and glass. Capacities of 15, 30, 60 and 120 litres are available. In addition to the standard type of disperser, larger specialised units with greater flexibility have been developed. The MASTERMIX HVS variable speed single-shaft and twin-shaft dispersers are available from 18 to 112 W or larger. Further development has taken place with the PMD disperser, which incorporates the double system of slow speed agitation and high speed dispersion; the machine is particularly suitable for handling difficult and heat sensitive materials. Vacuum operation is an optional extra. Machines of 1350, 2250, 4500 and 9000 litres capacity are available. An extensive range of slow speed and high speed tank mixers is available in sizes from 1350 to 9000 litres working capacity. MASTERMIX will design, manufacture and erect on site a complete manufacturing system, including all supporting steelwork and tank units.

METAL BOX LTD has recently launched the TD 1 automatic lid dispenser and demonstrated it on the Stand. It can be altered by the use of change-parts to accommodate 310, 410, 603 and 700mm diameter lids (0.5, 1, 2.5 and 5 litre tins). Change parts can be provided for other lid diameters up to 700mm.

MILLROOM ACCESSORIES & CHEMICALS LTD featured the Rotamix and Biotomix disperser/mixers. The Rotamix uses the well established rotor/stator principle; a hydraulic version is now available. The Biotomix works on the principle of two counter-rotating discs and relies on the shear between the blades and the mix to effect dispersion. It is primarily designed for high viscosity materials, but is being used increasingly for materials of lower viscosities. It is offered with single, dual or infinitely variable speeds. The Helix is a new type of high speed mixer, which gives effective turbulence by jet formation. Information was given on a range of vibratory sieves, conventional clip-on stirrers, mixers and storage vessels (see also under "Laboratory apparatus"). MILLROOM ACCESSORIES LTD stocks various types of grinding balls and lining bricks for ball mills, in spite of the prediction by some that their usage will cease.

The "Data-Paint" system developed by NORATOM-NORCONTROL AS is based on a new processing technology, combined with modern automation techniques. This provides benefits, such as optimisation of product formulation, savings in manpower, reduced waste of

materials, and reduction of stock. With past experience in the field of automation and computerised control, the company is able to offer know-how and hardware, from the instrumentation and modernisation of plant to the design and instrumentation of the new "Turn-key" process control system. The computer system on show at the Exhibition consisted of a computer, paper tape reader, Tandberg 22in TV, RGB monitor, Trackerball unit and operator's console.

RIO BEER MASCHINENFABRIK exhibited the C-ex machine for cleaning open top buckets.

HERBERT SMITH & CO. (GRINDING) LTD, which represents DIAF A/S and RIO BEER companies showed a range of mixing, filling, lidding and cleaning equipment. Information was given on the GABAU dry powder handling, dispensing, ball mill relining, and all types of grinding media. The company's own "Viscofill" volumetric filling machine is now available; it is pneumatically operated and has a filling range from 250ml to 3 litres per shot, accurate to  $\pm 0.5$  ml per 3 litres. The filling speed is adjustable between 5 and 15 shots per minute and a repeater device is available to give up to six continuous shots per cycle. The variable speed disperser "Vortexion HS8" is designed for mixing and dispersing viscous materials; it is available with 4 or 5.5 W motors, driving through an infinitely variable unit, to give between 500 and 3000 rpm. It operates with pans of 10, 20 or 30 gallons capacity, which rotate due to the action of the mix.

A. STRAZDINS PTY LTD demonstrated a full range of its new, improved designs of "Blendorama" colourant dispensers, including the single-pump 50ml capacity dispensing machine for small and medium stores, together with the 150ml capacity double-pump model and the larger 600ml capacity double-pump for bulk blending in factories. A prototype can piercer was shown. This can be used with any of the rotary dispensers and is an inexpensive device used to pierce a single hole, which may be sealed with a plastic plug after the tinting operation.

TORRANCE & SONS LTD provided full technical details of its full range of dispersing, mixing and particle size reduction equipment and offered advice on the application of TORRANCE equipment with emphasis on bulk production.

WENTWORTH INSTRUMENTS LTD exhibited a bench model of the RESEARCH INCORPORATED high intensity infrared conveyerised system. (See under Laboratory apparatus.)

## Pigments

ARCODE LTD offered a complete range of inorganic and organic pigments, iron oxides, pigment intermediates and dyestuffs of Romanian manufacture.

CHEMETRON CORPORATION exhibited a wide range of pigments and flushed dispersions for coating and ink applications; these included a flushed alkali blue, red and yellow shade transparent iron oxides developed specially for metallic finish and stain applications. Also shown were: phthalocyanine blues and greens and perylene red in press-cake form, newly developed for textile printing inks

and coatings; a new series of dry pre-dispersed pigments, containing 55 per cent pigment and designed to give greater flexibility in manufacture; a wide range of dry pigments, including lead-free pigments; and colour concentrates for plastics application, in a full range of colours.

DURHAM RAW MATERIALS LTD exhibited the DURHAM range of zinc dusts and gave details of particle size distribution in relation to surface appearance.

HERCULES POWDER COMPANY LTD showed a new range of lead-controlled chromes and a phthalocyanine blue FB 68 having unique properties, both from TEN HORN PIGMENTS BV. New developments are the fluorescent "Radiant R 303G" series for durable safety paints and the new N 100 series having improved fluorescent cost-effectiveness.

INDUSTRIAL COLOURS LTD featured the new 610 series of "Intense" pigments, which are considerably stronger than the normal INDUSTRIAL COLOURS "Flare" pigments. These pigments are new additions to the 610 range and do not replace existing products. The Flare series of aqueous fluorescent pastes include the 600 series for screen inks and paints based on mild solvents, the 610 series of finer particle sized, stir-in grades, and 810, a stir-in grade of high heat- and solvent-resistance, suitable for all paints, lacquers, inks, plastics and rubber. Information was available on the INDUSTRIAL COLOURS Flare U.610 series, the Flare 610 series and the Flare fluorescent aqueous pigment pastes.

JACOBSON VAN DEN BERG & CO (UK) LTD exhibited the HALOX PIGMENT DIVISION of HAMMOND LEAD PRODUCTS INC. range of white, anti-corrosive, non-toxic pigments suitable for solvent- and water-based metal and wood primers, the ANDRE VAN LERBERGHE high quality bronze and aluminium pigments for a wide range of uses, and grades of antimony oxide for fire retardant coatings manufactured by CPE METALLURGIQUE DE LA CAMPINE SA. The PODELL range of flushed and predispersed pigments for many applications were also shown.

LAPORTE INDUSTRIES LTD demonstrated its latest developments in the field of titanium dioxide pigments for the surface coating industry. A new grade "Runa REGL", designed for high gloss and high stability in water-based systems, was shown, and further information was provided on Runa RH 52 multipurpose titanium dioxide pigment, which gives high gloss and easy dispersion, and on the further developments in the range of chloride and sulfate process pigments.

MONTEDISON GROUP showed a wide range of the INDUSTRIAL PRODUCTS DIVISION's products of interest to the surface coating industry, amongst which were 11 grades of rutile and two grades of the anatase type titanium dioxide pigment, designed for general and special applications. A wide range of organic pigments manufactured by AZIENDE COLORI NAZIONALI AFFINI SPA were exhibited, including monoazo, bis-azo derivatives, aniline condensates, phthalocyanines and dioxyazines. A new range of co-precipitated organic/inorganic non-toxic pigments, the "Segnale" light yellows T3G and T2R has been introduced.



SILBERLINE LTD exhibited for the first time the full range of "Sparkle Silver" speciality pigments manufactured by its parent company in the USA. These included the acid resistant grades for use in automotive top coats and the 3500 grade for industrial (non-automotive) uses.

SUN CHEMICAL CORPORATION had "Ecology" as the theme of its stand at this year's Exhibition, and showed flushed colours designed for low energy and low emission heat-set inks and aqueous emulsion heat-set inks. New additions to the "Sunset" flushes introduced last year were also shown. Information on ink manufacture from flushed colours using filtration equipment was available. In the section on dry colours, new easily dispersible diarylide yellow and lithol rubine pigments, solid presscakes and high performance pigments, including quinacridone red, magenta and violet and carbazole violet were shown. Further developments in the micro-encapsulated pigments, introduced last year as development products, were illustrated.

TIOXIDE INTERNATIONAL LTD had the totally new type of pigment, "Spindrift", which was briefly described last year, as the central feature of its Stand at this year's Exhibition. Spindrift is supplied in a range of slurries to give easily made, matt and satin/silk latex paints of high opacity and film integrity. Its use and advantages were

demonstrated and descriptive booklets were available. In the field of orthodox pigments, Tioxide R-XG has been introduced to give superior gloss and outstanding opacity in gloss and semi-gloss latex paints and Tioxide R-TC 4 for pure whiteness in a range of finishes.

Pigment selection for epoxy, polyurethane and acrylic powder coatings were demonstrated, and the influence of powder size on film properties was shown.

## Resins

CHEMOLIMPEX has available resin esters, colophony based resins, colophony modified phenolic resins, including special grades for printing inks and maleic resins.

COLE CHEMICALS LTD exhibited a comprehensive range of hydrocarbon, terpene and coumarone resins manufactured by BRITISH STEEL CORPORATION and DRT of France, and showed the HERCULES INCORPORATED "Picco" resins.

DOW CHEMICAL EUROPE showed a bisphenol F/epoxy resin, based on diphenylol methane.

HERCULES POWDER CO. LTD showed its latest developments in phenolic resins for printing inks, Pentalyne 5303 and 5320, and the new composite resin Pexalyn 461 for use in inks. A new range of HERCULES hydrocarbon resins was described and in the field of water-thinnable coatings, a new range of "Picconal" resin dispersions has been introduced.

JACOBSON VAN DEN BERG & CO. (UK) LTD is able to supply the RICON high-vinyl polybutadiene resins, which cure to hard solids with excellent adhesion and corrosion resistance, and the CHEM-PLAST SPA range of phenolic resin dispersions for use as alkyd modifiers in fast drying primers.

JB LABORATORIES, including MICRON SERVICES, can provide plastic coatings for industry and the consumer.

MONTEDISON GROUP displayed its range of phenolic resins for surface coatings.

WARWICK CHEMICAL LTD exhibited its range of phenolic, maleic and alkyd resins for use in printing inks.

WORDSDALL CHEMICAL CO. LTD showed work done in its laboratories on resins and vehicles for the printing ink industry. The properties of the new chelating agent Estogel on an alkyd Estokyd A19, grinding medium Estovar 520 and on Estoset 600, a urethane modified complete ink vehicle were demonstrated. Another exhibit illustrated the effect on viscosity of solution of Surcprene rubbed resin, an Estokyd and Estovar vehicle of a standard CARLESS distillate and one of a low-emission type.

## Acrylic resins

MONTEDISON GROUP displayed its series of acrylic resins, including styrene-acrylics.

UCB SA exhibited two lines of non-polluting system, the "Ebecryl" resins for UV- and electron-beam curing and the "Uvecryl" resins, specially tailored for UV curing. Also shown were polyol polyacrylates, acrylated oligomers, polyester acrylates, polyurethane acrylates and epoxy acrylates. Demonstrations were given of typical UV-curable systems using the WALLACE KNIGHT Labcure system.

## Alkyd resins

ARCODE LTD is able to supply a range of alkyd resins of various oil lengths for decorative and industrial use.

CHEMOLIMPEX has available more than 30 types of alkyd resins.

MONTEDISON GROUP exhibited alkyd resins for use in paint.

WARWICK CHEMICAL LTD showed its range of alkyd resins for container and can coating and for wood finishes.

WORDSDALL CHEMICAL CO. LTD exhibited graphs and charts showing the results of laboratory work on its products (see under General Resins above).

## Amino resins

ARCODE LTD exhibited the "Urezit" range of amino resins.

CHEMOLIMPEX showed its range of amino resins for increasing the gloss of enamels.

MONSANTO EUROPE SA displayed its wide range of high solids content melamine/formaldehyde and urea/formaldehyde resins, the "Resimenes", which offer the versatility to give almost any film requirement. Resimenes are also designed for aqueous and high solids coatings, but can be used in conventional solvent based coatings to provide systems of medium solids content, in order to comply with continental requirements.

MONTEDISON GROUP exhibited its urea and melamine resin for use in paints.

## Emulsion and water-based resins

HERCULES POWDER CO. LTD showed its new range of "Picconol" resin dispersions for use in water thinnable formulations.

JACOBSON VAN DEN BERG & CO. (UK) LTD exhibited the AIR PRODUCTS AND CHEMICALS INC. high pressure co-and terpolymer ethylene/vinyl acetate emulsions for paints and adhesives, and also the "Vinac" polyvinyl acetate and "Vinol" polyvinyl ranges. Emulsified safflower oil PVO 44-0 is suggested for use with exterior semi-gloss emulsions.

MONTEDISON GROUP showed its range of vinyl acetate, pure acrylic and styrene/acrylic emulsions.

WARWICK CHEMICAL LTD showed water-based polyesters for textile coating applications.

## Epoxy resins

ARCODE LTD exhibited "Dinox" epoxy resins.

CHEMOLIMPEX is able to provide solid and liquid epoxy resins.

DOW CHEMICAL EUROPE exhibited the DER epoxy resin designed for use in ecologically unobjectionable coatings. New developments are designed to meet the powder coating industry's demand for thin films, faster reactivity, cure at lower temperatures and optimum shelf life.

## Polyamide resins

ARCODE LTD exhibited a series of polyamide resins.

JACOBSON VAN DEN BERG & CO. (UK) LTD showed the CHEM-PLAST SPA range of polyamide and polyamine resins for use as epoxy curing agents.

## Polyester resins

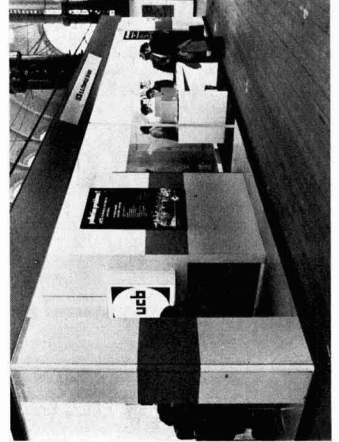
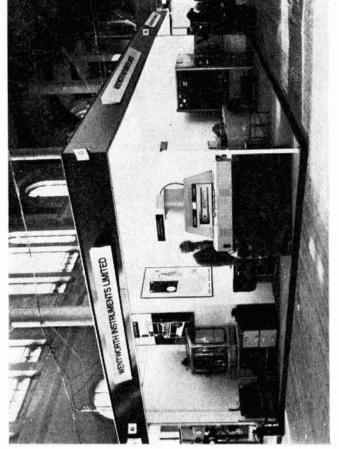
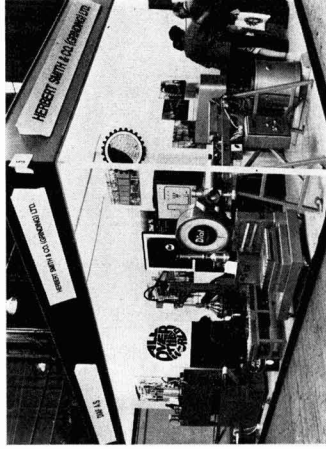
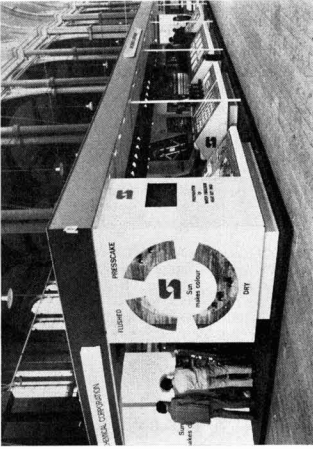
ARCODE LTD exhibited the "Nestrapol" series of unsaturated polyester resins.

UCBSA showed the "Crylcoat" polyester resin for powder coatings: 280 is a low hydroxyl value resin for use in urethane coatings, using blocked isocyanates as curing agents; 100M is a carboxylated polyester with an acid value of about 50, for curing essentially with triglycidyl isocyanurate; and 301M is intended for use in 50:50 combinations with epoxy resins.

WARWICK CHEMICAL LTD featured its polyester resins for chemically resistant cements, high gloss surface coatings and casting applications.

## Oils and fatty acids

JACOBSON VAN DEN BERG & CO. (UK) LTD displayed a range of products based on safflower oil and manufactured by PVO INTERNATIONAL INC., which included the conjugated oil 122-G for alkyd manufacture and emulsified safflower oil PVO 44-0 for water-based wood stains and exterior semi-gloss emulsion paints in conjunction with vinyl and acrylic latices. CEE-5 is a conjugated epoxy ester for vinyl floor coatings, masonry paints and water-based metal primers. The ZAPATA HAYNIE CORPORATION "Menhaden"



oil for alkyd production does not have the inferior drying, poor colour and objectionable odour of most fish oils.

## Solvents and plasticisers

JACOBSON VAN DEN BERG & CO. (UK) LTD gave information on the "Sadplast" plasticiser for water-based coatings.

## Technical journals, services and miscellaneous

Available on the Information Centre were details of membership of the Association, the Professional Grade and the Association's current publications: the *Journal of the Oil and Colour Chemists' Association*, which is published monthly and which has an unrivalled circulation among UK publications covering the surface coating industries; the 10-year index of the *Journal*, which includes Transactions and Communications covering the years 1966-1975; Paint Technology Manuals, Part 3 "Convertible Coatings" and Part 7 "Works Practice".

CIECH IMPORT AND EXPORT OF CHEMICALS LTD exhibited alkyd resins, inorganic pigments and a wide range of paints, which included the latest "Oliva" marine paints, electrically insulating paints, filling pastes, paints and lacquers for the building industry, quick drying wood lacquers and epoxy powder coatings.

DESERT SUNSHINE EXPOSURE TESTS INC showed slides illustrating the various methods of conventional and accelerated weathering testing, with emphasis on the solar concentrators "Emma" and "Emmaqua", which give an eightfold acceleration of conventional outdoor tests on similar or sub-tropical sites.

JB LABORATORIES, including MICRON SERVICES, provides a liquid mixing, homogenising and packaging service for industry.

The PAINT RESEARCH ASSOCIATION provided its fibre optics colourimeter for display on the Technical Education Stand.

POLYMERS, PAINT & COLOUR JOURNAL continues its service of technical and commercial news and comment on current developments in the polymer and colour using industries. It continues to organise symposia on a variety of topics, especially the technico-commercial aspects.

WHEATLAND JOURNALS LTD exhibited copies of "Paint Manufacture", now published ten times a year, which gives information on all aspects of manufacture and basic raw materials. Copies of Industrial Finishing and Surface Coatings Journal were displayed. The 1976 Industrial Finishing Industries Manual is available, and the purchase price includes a year's subscription to Industrial Finishing and Surface Coatings Journal. Copies of the magazine Process Biochemistry were also available on the Stand.

## OCCA-28 Review

(Continued from page 183)

are drawn from all parts of the world to the focal point of the Exhibition and the subsequent out-flowing of information which has been displayed and discussed. Invitations to exhibit will be despatched in May 1976 and the closing date for applications will be 1 October 1976.

Any company which has not previously received an invitation to exhibit and wishes to do so should write at once to the Director & Secretary, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex, HA0 2SF England (telex: 922670 OCCA Wembley).



The motif for OCCA-29, designed by Robert Hamblin, uses inward-pointing arrows to symbolise how exhibitors and visitors are drawn from all points of the compass to the Exhibition. The heads of these 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.

# Report of Council Meeting

A meeting of Council took place at the Great Northern Hotel, London, N1 on 1 April 1976 with the President, Mr A.T.S. Rudram in the chair. There were 18 members of Council present.

It was reported that arrangements for the Annual General Meeting to be held on 25 June were complete.

The names of Presidents of other societies who had accepted the Council's invitation to be present at the Dinner Dance on 14 May were given to the Council and arrangements made for the Reunion Dinner for past and present members of Council, which would take place on 13 October 1976, following the Council meeting held earlier on that day.

Reviews were given on the 1976 Exhibition and the arrangements for the 1977 Exhibition, which will take place at Alexandra Palace from 22 to 25 March 1977.

The totals of Members in arrears with subscriptions were given to the Council, which noted with pleasure that the number in this category in the General Overseas Section was very much lower than at a comparable date in 1975 and that the numbers involved in the UK and Irish Sections were almost equivalent to those at the April 1975 Council meeting.

The Honorary Treasurer reported on the meeting of the Finance Committee which had been held on 11 March and introduced the accounts for the year which were

adopted by the Council for circulation with the Annual Report.

All members of Council were asked to ensure that the Personnel Departments within firms were fully aware of the classified advertisement facilities in the Association's *Journal*.

It was reported that the Decennial Index of the *Journal*, covering the years 1966-1975, had now been printed and a leaflet would be placed in the April issue of the *Journal*.

It was further reported that the Exhibition Review would appear in the May issue of the *Journal* and that the revision of "Introduction to Paint Technology" had reached a position where it was hoped to report to the July Council meeting that printing of the third edition was in progress.

A report was given on the number of papers which had been offered for the Association's 1977 Conference.

The Council were informed that the Professional Grade Committee had admitted a further two Fellows and eight Associates.

It was reported that the petition from the Ontario Branch of the London Section had been received and Council were able to confirm that the Branch would be accorded Section status from the date of its Annual General Meeting in April. Council were pleased to learn that the Honorary Treasurer

of the Ontario Branch, Mr W. Fibiger had visited the Exhibition and had discussed the arrangements for the setting up of the Section with the Director and Secretary, the Honorary Treasurer of the London Section, Mr D. Bannington, and the Honorary Secretary of the London Section, Mr H.C. Worsdall, who would be attending the Annual General Meeting of the Branch and would be making a presentation to the new Section on behalf of the London Section.

Reports were received of Section activities from the various Sections and items arising from these were discussed by Council in detail. It was noted with pleasure that the Scottish Section had received a request from the company employing a former Chairman of the Section, the late Jimmy Miller, that they be allowed to make an addition to the Presidential Insignia to commemorate his service to the Association. The President reported that he and the Director and Secretary had discussed the suggestion and submitted to Council a proposal to incorporate a Scottish thistle in gold and semi-precious stones. The Council approved this proposal and it was hoped that the addition to the Presidential Insignia would be incorporated before the next session, commencing September 1976.

There being no other business the President thanked members for their attendance and declared the meeting closed at 3.35 p.m.

## Jordan Award

This award was instituted by the late Mrs M. R. Jordan in memory of her husband Dr L. A. Jordan, who was President of the Association 1947-49 and an Honorary Member, and who died in December 1964. The Committee invites applications for the fourth award of £100.

The rules of the Award are:

1. The Award will be made for the best contribution to the science or technology of surface coating by a Member of any nationality working in either the academic or industrial field who is under the age of 35 at the date of application.

2. The final date for submission of applications will on this occasion be 31 December 1976 and it is hoped to present the award at the 1977 Association Conference.

3. The selection of the recipient of the Award will be made by a Committee under the chairmanship of the Association's Hon. Research and Development Officer.

4. There will be two methods of application. First, by the submission of a paper describing original work by the candidate which is offered for publication in the *Journal* or has been so published during application. The alternative method will be by recommendation by a superior for work which for reasons of commercial secrecy cannot be published; in this case the candidate will be expected to submit a dissertation on a topic relating to his work and demonstrating his superior knowledge of the principles thereof. The Award is for individual merit and clear evidence of the candidate's own contribution will be required if a paper is offered under joint authorship.

5. Applications should be addressed to the Director & Secretary at the Association's offices.

## News of Members

Dr F. Dalton, an Ordinary Member attached to the General Overseas Section and an Associate in the Professional Grade, has taken charge of the Pigments Division of Kemisk Værk Koge A/S in Denmark (a member of the Sadolin and Holmblad group).

Dr Dalton was previously marketing director of the Pigments Division of CIBA-GEIGY (UK) Ltd, and served on the Manchester Section Committee when attached to that Section.

The Pigments Division of Kemisk Værk Koge A/S manufacture a wide range of phthalocyanine and azo organic pigments and pigment preparations.

Mr J.G. Goodrum, an Ordinary Member attached to the Scottish Section, has taken up an appointment as group technical manager for Stewart Wales Sommerville Ltd, a rapidly expanding independent surface coatings manufacturing organisation based in Scotland.

Mr Goodrum was previously works manager with Camrex (Holdings) Ltd and served for a time as a member of the Newcastle Section Committee, when attached to that Section.

Mr A. Ridley, an Ordinary Member attached to the Newcastle Section, has been appointed general sales manager of the Protection special coatings division of Berger Paints. Mr Ridley was previously a regional sales manager and has spent a number of years with Berger (and before then with British Paints).

The Protection division provides technical consultancy and sophisticated special coatings for specifiers and builders of structural steel and concrete.

## Manchester Section

### AGM and supper evening

Some 80 members attended the Section AGM, which was held at the Albion Restaurant, Manchester. After the formal proceeding, a supper was enjoyed followed by an entertainment in which a team, three ex-Chairmen, competed in a quiz against three "challengers". The quizmaster was Dr F. M. Smith. Some very erudite questions were asked, and the answers were on occasion actually correct. Final score—Chairmen 18, Challengers 15, Audience 30. The match was abandoned due to dryness of pitch as last orders had been called.

## Register of Members

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

### Ordinary Members

CARAVIAS, PETER, MSc, Sadolins Paints (Cyprus) Ltd, PO Box 1285, Nicosia, Cyprus. (*General Overseas*)

CODD, STANLEY HUGH, LRIC, Stone Lea, Dale Road North, Darley Dale, Derbyshire.

(*Midlands Section—Trent Valley Branch*)  
DYSON, ALLAN FREDERICK, LRIC, 11 Eastleigh Grove, Bradford, West Yorks BD5 9DR. (*West Riding*)

GRAY, ALAN, Shell Oil NZ Ltd, Chemicals Dept, Box 2091, Wellington, New Zealand. (*Wellington*)

LEECH, BRIAN CIARAM, BSc, 34 Tramore Heights, Tramore, Co. Waterford, Ireland. (*Irish*)

MCDUGALL, EDWARD SHERIDAN, 4190 Afton Court, Burlington, Ontario, Canada. (*London Section—Ontario Branch*)

PATEL, SHRISH, BSc, 1455 Lawrence Avenue West, Apt 1503, Toronto, Ontario M6L 1B1, Canada.

(*London Section—Ontario Branch*)  
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SMEDMOR, JOHN HENRY, 69 Mackay Avenue, Blairgowrie, Randburg, Transvaal, South Africa. (*South African*)

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WILLIAMS, CHRISTOPHER BRIAN, Plascon Evans Paints, PO Box 10, Luipaardsvei, Krugersdorp, South Africa. (*South African*)

### Associate Members

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GILLESPIE, KEN, National Chemical Co. Ltd, 42 Lower Leeston Street, Dublin, Ireland. (*Irish*)

MCINERNEY, NOEL ANTHONY, 53 Jamestown Road, Inchicore, Dublin 8, Ireland. (*Irish*)

MONTEIRO, JOAQUIM JOSE HELIODORO, Asian Paints (India) Ltd, Post Bag No. 7318, Bhandup, Bombay, India 400 078.

(*General Overseas*)

### Registered Students

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HARDIE, IAN WILLIAM, 2 Chester Road, Chigwell, Essex IG7 6AJ. (*London*)

TURTON, ALAN MAXWELL RALPH, 31 Brick Street, Flanshaw, Wakefield. (*West Riding*)

WEBSTER, IAN ANDREW, 42 Spring Avenue, Gildersome, Morley, Leeds. (*West Riding*)

## Forthcoming Events

Members are reminded that the Association's Biennial Dinner and Dance will be held on Friday 14 May at the Savoy Hotel, London WC1 at 7.00 for 7.30 p.m.

The West Riding Section Symposium "Exporting paints and similar products" will be held in Harrogate on 24 and 25 June (see page ii).

Full details of Section meetings for the 1976/77 session will be appearing as usual in the August issue of the *Journal*.

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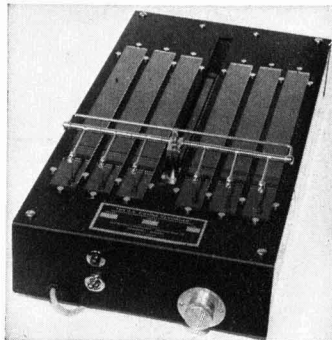
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A reprint of the full regulations for admission to the Professional Grade and application form may be obtained by sending a stamped, self-addressed envelope, marked "Professional Grade leaflet" in the top left-hand corner, to the Association's offices at the address on the Contents page of this issue. It is felt that some overseas Members, in particular, might encounter difficulties contacting the required number of sponsors and any applicant who finds himself in this position is advised to write to the Director & Secretary of the Association in the first instance.

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Classified Advertisements are charged at the rate of £3.00 per cm. Advertisements for Situations Wanted are charged at 75p per line. A box number is charged at 50p. They should be sent to C. A. Tayler, BSc, Assistant Editor, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF. JOCCA is published EVERY month and Classified Advertisements can be accepted up to at least the 12th, and in exceptional circumstances the 20th of the month preceding publication. Advertisers who wish to arrange for an extension of the copy deadline should contact the Assistant Editor, Mr C. A. Tayler, at the address given above (telephone 01-908 1086, telex 922670 OCCA Wembley).

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## PERSONAL

LESLIE SILVER of SILVER PAINT AND LACQUER CO. LTD would like to take this opportunity of thanking his many friends in OCCA for their good wishes to his wife Anita during her recent stay in hospital. The messages were a great comfort during a difficult time.

He is also delighted to report that Anita is now at home, and making a good recovery.

**ASSOCIATION DINNER  
and DANCE**

**Savoy Hotel, London WC2**  
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**OCCA-29 TECHNICAL EXHIBITION***Official Guide*

The Exhibition Committee offers advertising space in the *Official Guide* to the Exhibition, which has proved to be a very popular advertising medium, not only for exhibitors but also for companies who were not showing at a particular Exhibition. Advertising space in the 1977 *Official Guide* will not, therefore, be restricted solely to those to whom space is allocated for the 29th Technical Exhibition, and companies who will not be applying for stand space may well wish to secure advertising space in this important medium.

This unique publication will be circulated to all members of the Association, both at home and overseas, and as far as possible to all consuming companies in Great Britain. They will also be sent to those applying as a result of the Association's wide-spread publicity. The advantages of an advertisement in the *Official Guide* need hardly be stressed, since it will contain details of each Exhibitor's stand and constitutes a summary of those recent technical developments which will be shown; consequently, it will be read widely and kept for reference.

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## INDEX TO ADVERTISERS

### A

Alliance Dye & Chemical Co. Ltd	..	..	vi
Ashby, Morris, Ltd	..	..	iii

### B

Banner, Samuel, & Co. Ltd	..	..	xvi
Boulton, William, Ltd	..	..	iv

### C

Carless Solvents Ltd	..	..	xii
CIBA-GEIGY (UK) Ltd (Inks)	..	..	xv
CIBA-GEIGY (UK) Ltd (Paints)	..	..	Cover
Ciech Polifarb	..	..	ii
Cory, Horace, & Co. Ltd	..	..	viii
Crosfield, Joseph, & Sons Ltd	..	..	xiii

### E

English China Clays (Sales) Co. Ltd	..	v
-------------------------------------	----	---

### G

Glen Creston Ltd	..	..	Cover
------------------	----	----	-------

### H

Highgate & Job Ltd	..	..	x
--------------------	----	----	---

### I

ICI Organics Division	..	..	ix
-----------------------	----	----	----

### M

Metchim & Son Ltd	..	..	xx
Mickle Laboratory Engineering Co.	..	..	xvi
Monsanto	..	..	xi

### S

Sachtleben Chemie GmbH	..	..	xiv
Sandoz Products Ltd	..	..	Cover
Sheen Instruments (Sales) Ltd	..	..	x
Sub-Tropical Testing Services Inc.	..	..	iv
Surface Treatment Show	..	..	xvii

### U

UCB sa, Chemical Division	..	..	i
---------------------------	----	----	---



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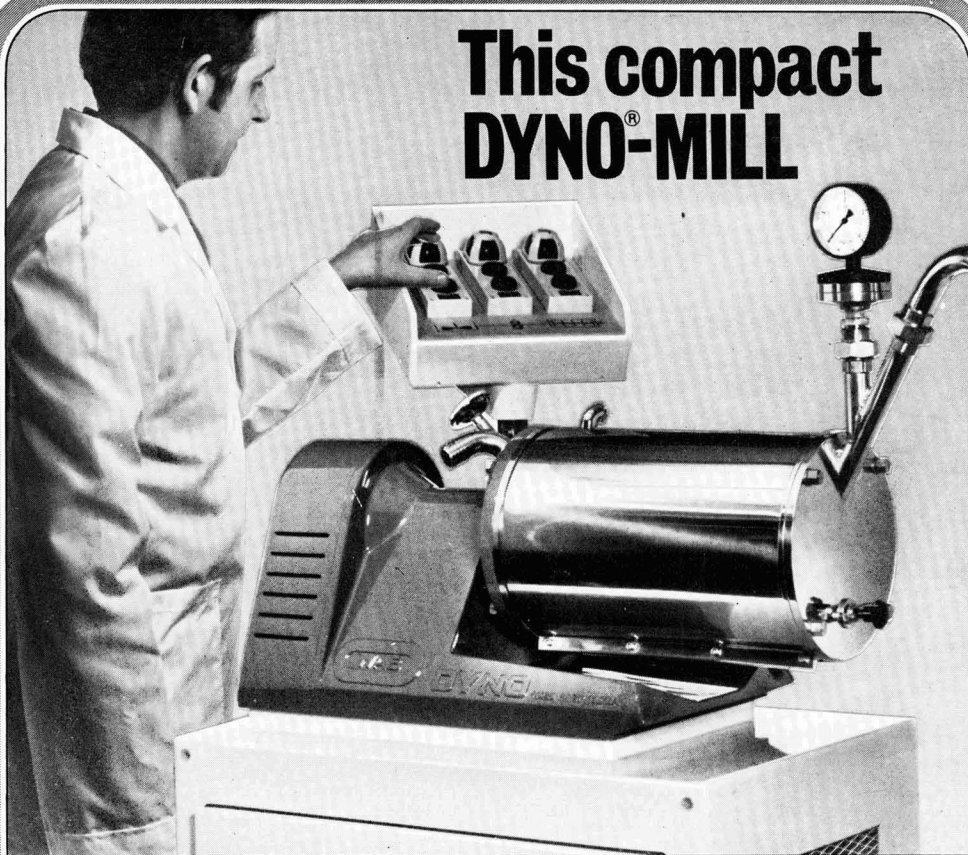
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